

YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



In situ measurements of sea-surface film potentials

by P. M. Williams,¹ E. S. Van Vleet² and C. R. Booth¹

ABSTRACT

A sensitive electrode system has been built for measuring *in situ* sea-surface potentials from a mobile platform. The initial results of this study point out the patchy nature of the surface films in some "slick" areas as well as in non-"slick" regions, and illustrate the potential usefulness of this technique in measuring film formation and alteration rates.

1. Introduction

The ubiquitous occurrence of organic films at the sea surface is due primarily to surface-active organic compounds derived from marine plants and animals, and secondarily to surface-active compounds introduced from the atmosphere and from petroleum operations. Regardless of the source, these organic films mediate air-sea energy exchange by their effects on capillary wave damping, insolation and water evaporation. Yet little is known of the composition of these films, chemically or biologically, and of their rates of formation, alteration and disappearance. This work on the measurement of *in situ* surface potential (ΔV_s) is part of an experimental program designed to measure the *in situ* rates of formation of sea-surface films and to gain insight into the changes in composition of the films as they are sequentially generated in the laboratory and *in situ*.

Previously reported measurements of ΔV_s have been restricted primarily to laboratory systems where the seawater samples were collected by screens, slides, or in bottles and brought back to the laboratory (Jarvis, 1967; Jarvis *et al.*, 1967; Baier *et al.*, 1974). Such surface film and seawater samples are subject to alteration through physical mixing, formation of particulate organic matter, and biological transformations. *In situ* measurements of ΔV_s taken from a skiff, using a floating electrode system similar to that used in this study, have been reported for a lake in West Virginia and for coastal waters off San Diego, California (Bultman *et al.*, 1963). These results are discussed later in more detail.

This paper describes a portable electrode system for measuring surface potentials

1. Institute of Marine Resources, A-018, University of California, San Diego, La Jolla, California, 92093, U.S.A.

2. Present address: Department of Marine Science, University of South Florida, St. Petersburg, Florida, 33701, U.S.A.

in situ from a self-contained, mobile sampling platform, and gives some results for ΔV_s measurements on surface films off southern California and in the southern Gulf of California. Also included are data on the concentration of total organic carbon and bacteria in some of the films and in the corresponding 10 cm subsurface waters.

2. Definitions

The surface potential (usually written as ΔV_s and measured in terms of Volta potentials; Gaines, 1966) of an organic monolayer spread on seawater may be defined as the difference in the measured potential between a "clean" seawater surface and the same seawater surface covered by an organic film. A "clean" seawater surface may be further defined as that for organic carbon-free seawater or for natural seawater wiped free of existing films. If an insoluble monolayer having a permanent dipole is spread on seawater, then the potential difference at the interface will be changed according to the dipolar characteristics of the monolayer and its interaction with the seawater system. The relationship between the dipole moment (μ) of the monolayer component (i) and ΔV_s is given by the Helmholtz formula (1) (Davies and Rideal, 1963), modified to include the electrostatic charge (ψ) on the film molecules, if present.

$$\Delta V_s = 4\pi n_i u_i + n_i \psi \quad (1)$$

For a single component system ($i=1$) where n = the number of molecules of film material per cm^2 , μ can be expressed as $(\bar{\mu} \cos \theta)D^{-1}$, where $\bar{\mu}$ = the average dipole moment of n molecules, θ = the angle the dipole makes with a line normal to the water surface, and D = the dielectric constant of the film. In a single component system, equation (1) then becomes

$$\Delta V_s = \frac{4\pi n \bar{\mu} \cos \theta}{D} + n \psi \quad (2)$$

The electrostatic charge, ψ , becomes important in seawater systems where ionized monolayers may be present, e.g. fatty acids and/or nitrogenous bases. Interactions of these ionized systems with seawater often have greater effects on ΔV_s than the dipole moment of the film material. In monolayers carrying no net electric charge (e.g., long chain alcohols or esters), $\psi = 0$, and equation (2) reduces to

$$\Delta V_s = \frac{4\pi n \bar{\mu} \cos \theta}{D} \quad (3)$$

Although the dipole moment of a film forming molecule may theoretically be calculated from ΔV_s measurements, in practice, the agreement between such measurements and the intrinsic dipole moment of the molecule is poor; μ (intrinsic) $\cong 10\text{-}30 \times \mu$ (V_s) (Gaines, 1966). Measurements of ΔV_s , especially in seawater systems, are most useful in comparison to ΔV_s values in known systems (Van Vleet and Williams,

1979), in relative measurements between different seawater samples, and in film formation and alteration studies on *in situ* films.

The surface film pressure (γ_f), given in this paper for *in situ* films, is defined as being equal to the reduction in surface tension of a pure liquid (in this case, seawater) by a molecular film spread on the liquid (Adam, 1941).

$$\gamma_f = \gamma_{sw} - \gamma_{sf} \quad (4)$$

where γ_{sw} is the surface tension of "clean" seawater ($\sim 73 \times 10^{-3} \text{ N m}^{-1}$) and γ_{sf} is the surface tension of the seawater covered by an organic film. Surface film pressure is a function of the size, packing, number, orientation, and chemical nature of the molecules at any given compression (Adam, 1941). In this work γ_f was measured with spreading (piston) oils (Adam, 1937). Piston oils, used under optimum conditions, are accurate to $\pm 0.5 \times 10^{-3} \text{ N m}^{-1}$.

It should be noted that the ΔV_s measurements are approximately 10 times more sensitive than the corresponding γ_f values in detecting the presence of organic films. This discrepancy is largely due to the experimental limitations on calibrating the piston oils and to the fact that an intact monolayer may be sensed by ΔV_s measurements, but on water its molecules must be compressed sufficiently to lower the surface tension ($\sim 0.5 \text{ dynes cm}^{-1}$) before piston oils can be of use.

3. Experiment

ΔV_s electrode. The ionizing electrode system used here was a modification of the ones originally constructed by Bewig (1964) and Jarvis *et al.* (1967). It allows continuous monitoring of ΔV_s with time, provided the electrode does not become wet (with seawater) and that it is calibrated before and after each series of measurements.

The electrode consists of 90 μCi of ^{241}Am sealed in a gold-silver foil (Amersham/Searle). The foil is soldered to a copper disc electrically connected to the input of an FET "electrometer" type operational amplifier configured as a voltage follower. This entire assembly is housed in a 8.0 cm diameter aluminum container with the ^{241}Am electrode mounted in a 0.5 cm thick Teflon insulator such that the ^{241}Am foil is exposed at the bottom. The entire bottom surface, except for the ^{241}Am foil, is then painted with Teflon paint (Camie TFECOAT, formula 2000) and the electronics potted using SYLGARD[®] 184 silicone encapsulating resin. The electrode is positioned 0.5-2.0 cm (optimum 1-1.5 cm) above the seawater surface thereby ionizing the air-gap. The electrical reference to seawater is made with a 1.17 mm diameter silver wire (cleaned with 5% HNO_3 and soaked 48 hr in seawater to establish the Ag-AgCl junction).

Figure 1 shows the electrical circuit and potentials contributing to the output voltage (V_{out}). The equation for V_{out} is:

$$V_{\text{out}} = I_b (R_{\text{air}} + R_{\text{H}_2\text{O}} + R_p) + e_0 + V_R + V_s + V_A \quad (5)$$

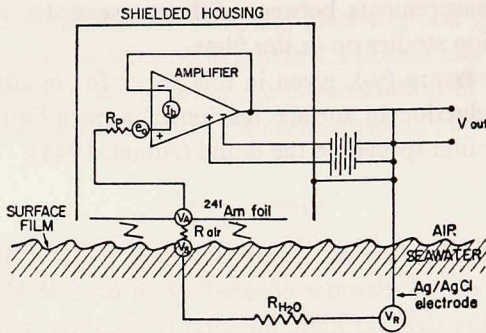


Figure 1. Circuit diagram of ^{241}Am electrode measuring system.

where I_b is the amplifier bias current ($<10^{-11}$ A), $R_{\text{H}_2\text{O}} = <100 \Omega$, $R_p = 10^8 \Omega$ (this is to limit static charge currents into the amplifier and can be considered negligible here), e_0 (<10 mV) is the amplifier offset voltage, V_R is the silver-silver chloride reference electrode potential, and V_A is the ^{241}Am electrode surface potential. Considering V_R and V_A to be constant, and I_b and e_0 relatively small, the change in the amplifier output (ΔV_{out}) is identical to the change in the surface potential (ΔV_s) such that:

$$\Delta V_{\text{out}} = \Delta V_s \quad (6)$$

An important result of the integral nature of the electrode and amplifier was that the assembly was largely insensitive to electrostatic interference due to movement around it and thus no further shielding was necessary. In practice, the amplifier output is recorded on a battery-driven strip-chart recorder and also displayed on a digital millivoltmeter. The precision of the V_s measurements is ± 2 mv in the laboratory and ± 5 mv in the field.

Calibration of the electrode system is done by placing it in an insulating chamber 1 cm above a gold-coated copper disc 5 cm in diameter. The disc is connected to a high stability reference voltage (± 1 mv) that can be switched between 0 and 225 mv relative to the amplifier ground. The output values from the electrometer at both 0 and 225 mv are recorded in order to monitor electrode drift, and thus allow normalization of all readings to the same zero potential. This drift in absolute output is attributable to changes in the input offset voltage and current in the amplifier, and to changes in the surface potential of the ^{241}Am electrode itself. These surface potential changes on the electrode surface are due to coating with sea salts, surface moisture, and organic films.

The corrected values of V_s (ΔV_s , Table 1) are obtained by subtracting the voltage of the standardization chamber at zero potential from the measured *in situ* V_s values. Further normalization of the corrected *in situ* V_s values to organic carbon-free seawater ($>99\%$ carbon-free as obtained by high energy ultraviolet oxidation

Table 1. *In situ* surface potential, film pressures and other data for surface films at stations in the Gulf of California and off the southern California coast.

Station	Location	Date-Time	<i>In Situ</i> ΔV_s (mv)	ΔV_s (mv)	Max-Min (mv)	<i>In Situ</i> γ_f $N m^{-1} \times 10^{-9}$	Observations
1	24° 51.7'N 110° 33.0'W San José Is.	Mar. 23, 1979 0730-0830	max = 545 min = 300	max = 435 min = 190	245	0.5-1.5	Choppy. In and out of slick.
2	"	Mar. 24, 1979 0500-0830	max = 435 min = 200	max = 295 min = 60	235	7-9	Calm. In slick. γ_f out of slick = 0.5-1.5.
3	"	Mar. 25, 1979 0500-0700	max = 430 min = 410	max = 365 min = 345	20	>16.9	Calm. Slicks breaking up with time. γ_f out of slick 0.5-1.5.
4	"	Mar. 25, 1979 2030-2330	max = 350 min = 130	max = 255 min = 35	220	—	Very Calm. Night, probably in slick.
5	32° 52.5'N 117° 15.0'W La Jolla Cove	June 20, 1979 0700-0800	max = 335 min = 280	max = 235 min = 180	55	6.0-7.2	Calm. In strong banded slick.
6	"	June 20, 1979 0900-0930	max = 425 min = 225	max = 315 min = 115	200	0.5-1.5	Light wind chop. Out of slick.
7	"	June 20, 1979 0930-1000	max = 480 min = 380	max = 417 min = 310	107	1.0-1.5	Calm. In kelp bed.

of filtered, surface seawater; Armstrong *et al.*, 1966) can be done by subtracting 150 \pm 10 mv from the ΔV_s values given in Table 1. The 150 \pm 10 mv represents the

average surface potential of organic carbon-free seawater measured in the laboratory with the same electrode system used in the field.

Sampling and measurement platform. A mobile platform for carrying out *in situ* studies on the chemistry and microbiology of surface films was constructed such that contamination problems would be minimized. The platform (R.V. *Adam*) is similar to that built by Fasching *et al.* (1974) for studies on sea to air transport of metals.

The pontoons and frame members of a 5.5 m (18 ft.) "Hobie-Cat" were the basic floating and support units. An all-wood (primarily 1.9 cm [$\frac{3}{4}$ inch] plywood) removable platform was fitted onto the pontoons and painted with teflon paint to suppress contamination by organic matter. The platform is powered by a ~ 2 horsepower "Brute" H-1 electric motor (Arnold Industries, Inc.) using two 12 v high amperage storage batteries. With 3 people on the platform, the free-board is 30-38 cm and thus screen sampling for films and other types of sampling can be easily accomplished. The pontoons are wiped clean with methanol and/or hexane when necessary. A 76 \times 91 cm well was cut into the forward end of the platform to allow a wooden-framed, lucite-panelled box to be raised and lowered into the well. The box was open on the top and bottom and when lowered was immersed ~ 36 cm into the seawater. Judging from visual experiments with fluorescein dye, there was significant turbulence in this trapped parcel of seawater. For example, fluorescein dye injected 30 cm below the surface normally dispersed throughout the trapped seawater in the order of 5 min. The initial ΔV_s measurements have been made under these turbulent conditions (as opposed to completely trapped or turbulence-suppressed water parcels) as they most closely resemble the *in situ* situation.

The ^{241}Am and silver electrodes were fitted into a second wooden-framed lucite-covered floating box 5 cm thick which just fitted into the large box in the well (clearance was 1-2 cm on all sides). Thus, the height of the ^{241}Am electrode above the sea surface remained relatively constant (at 1.5 cm) as the box floated with changes in water height. In addition, the lucite covers protected the surface film from possible atmospheric inputs of surface-active material. The boundary conditions imposed by the walls of the fixed and floating boxes can cause unpredictable perturbations on the *in situ* films, such as multilayer formation and possible scavenging of film material by the teflon-coated, wooden frame of the floating box. In this sense, the use of the term *in situ* in this paper is so qualified. For wiping the surface films off the trapped seawater, 28 cm, white, paper roll-towels were attached to a T-bar, and the surface wiped 2-3 times while the electrode holder was raised. (Surprisingly, these particular towels do not give a significant blank using organic carbon-free seawater as a control.) The electrode holder and electrodes were then put back down on the water, usually within 5-10 sec after wiping the surface. Bubbling was carried out with compressed air (freed of organic matter by passage through activated charcoal) introduced about 10 cm below the surface at the bottom corner

of the large box. The rate was $35 \text{ cm}^3 \text{ min}^{-1}$ where the bubble diameters were $\sim 0.3 \text{ mm}$ at the frit. These diameters are at the higher end of the range of bubble diameters produced in the ocean by breaking waves or whitecaps (Blanchard and Woodcock, 1957). ΔV_s measurements in the box are limited by sea state, generally being impossible at sea states >2 , due to seawater splashing on the ^{241}Am foil.

Film pressure measurements. These were made according to Barger's technique (Barger *et al.*, 1974) after the ΔV_s work was completed. A series of piston oils ($0.16.9 \times 10^{-3} \text{ N m}^{-1}$ spreading pressure) were compounded from various admixtures of 0.05-1.0% dodecanol with white paraffin oil (Saybolt viscosity = 180-190 at 100°F), and calibrated in a Langmuir trough against a stearic acid film spread on organic carbon-free seawater at pH 3 (Adam, 1937; Zisman, 1941). Pure sorbitan monoleate ($40.9 \times 10^{-3} \text{ N m}^{-1}$ spreading pressure) was used to detect γ_f values >16.9 and $<40.9 \times 10^{-3} \text{ N m}^{-1}$.

The *in situ* film pressure is estimated by throwing toothpicks dipped in piston oils of increasing surface tension into the seawater until the piston oils just begin to spread against the *in situ* film. This brackets the *in situ* film pressure to $\pm 0.5 \times 10^{-3} \text{ N m}^{-1}$ (Table 1).

Total organic carbon and total bacteria measurements. The total organic carbon (TOC) equals the particulate plus dissolved organic carbon and was measured by wet oxidation with persulfuric acid (Menzel and Vaccaro, 1964) of unfiltered samples. The film samples (3.2 ml) were collected with a 7 cm by 14 cm calendared, 16 mesh, stainless-steel screen (Garrett, 1965) which had 53% open area. The $10 \text{ cm} \pm 1 \text{ cm}$ subsurface samples (5 ml) were taken with a 10 ml syringe fitted with a clean, sterile disposable glass pipette. These samples were collected in the box after the V_s measurements had been taken. The ratio of the total film area to the area sampled was 46:1. All of the TOC samples were frozen at -20°C and analyzed in the laboratory two weeks later. The results for the film samples were corrected for the subsurface water entrained on the screen, assuming its TOC concentration was identical to that of the 10 cm subsurface water, and further assuming that the film thickness was $150 \mu\text{m}$ (Garrett, 1965). In practice the subsurface water comprised 6% of the total film sample collected.

Total bacteria (living and dead) were enumerated by epifluorescent microscopy (A. F. Carlucci, private communication) on formalin-fixed surface film and 10 cm subsurface water samples collected in the same way and at the same time as those for TOC determinations.

4. Results and discussion

The results (Tables 1 and 2, Figure 2) were chosen to represent differing oceanographic regimes and film situations encountered off southern California and at two anchor stations near San José Island in the southern part of the Gulf of California.

Table 2. TOC and total bacteria measurements for *in situ* films (*SF*) and 10 cm subsurface waters (*SS*) at stations 1, 2 and 3, Table 1.

Station	TOC (mg C l ⁻¹)			Total bacteria (cells ml ⁻¹ × 10 ⁻⁹)		
	<i>SF</i>	<i>SS</i>	<i>SF/SS</i>	<i>SF</i>	<i>SS</i>	<i>SF/SS</i>
1	1.47	1.11	1.3	1.5	1.4	1.1
2	3.96	0.87	4.6	3.7	2.4	1.5
3	2.15	1.10	2.0	2.6	3.2	0.8
3	2.68	0.90	3.0	6.4	1.9	3.4
(Bubbled 10 min)						

The former location is subject to oil contamination from various natural and anthropogenic sources, but at the time of measurement appeared free of gross contamination (bottom depth = 15-90 m). The stations near San José were in 3 to 60 m of water in the lee of the island. There were dense populations of zooplankters, fishes, etc., in these Gulf waters although the phytoplankton stocks were not extraordinarily high (1-1.5 mg chlorophyll-a m⁻³) due to grazing. Heavy surface "slicks" were present at most times in the Gulf but tended to dissipate when the NW winds exceeded about 10 to 15 knots. The ΔV_s and γ_f measurements were taken from the platform, launched between 0500-0600 from the R.V. *New Horizon*. The wind normally increased at 1000-1100 and prevented further ΔV_s work. Locally, off La Jolla, the platform was launched through the surf.

The values listed in Table 1 for surface potential are designated *In Situ* V_s for voltages directly measured where *max* and *min* are maximum and minimum V_s values taken from the strip chart records and refer only to the initial *in situ* film measurements before wiping or bubbling. The ΔV_s values (Table 1) are the *In Situ* V_s values corrected for electrode zero potentials and are not necessarily the same as the surface potential differences between seawater with and without films present. Subtracting 150 mv from the ΔV_s values in Table 1 gives surface film potentials relative to organic carbon-free seawater. The ΔV_s values are about 50-100 mv higher than those found for compressed monolayers of known compounds spread on organic carbon-free seawater (e.g. collagen, albumin, alginic acid, fulvic acid, and various lipids; Van Vleet and Williams, 1979), while the surface film potentials relative to organic carbon-free seawater are 50-100 mv lower than those of the monolayers of known composition.

In situ γ_f values were measured sporadically, and not always at the same time as the ΔV_s work was underway (due to possible contamination of the platform by piston oils). Thus, the γ_f numbers in Table 1 represent the true film pressure differences only at the approximate time and place the ΔV_s measurements were made. Some heavy slicks in the Gulf had γ_f values between 16.9 and 40.9 × 10⁻³ N m⁻¹ in areas where the wind apparently caused "rafting" and compression of films.

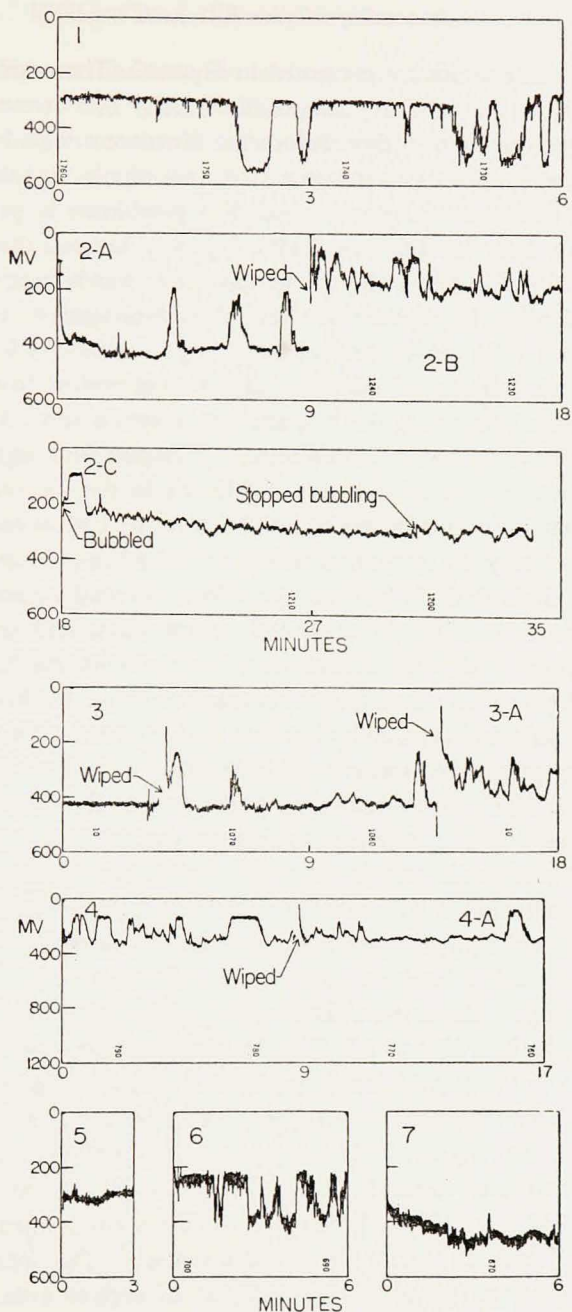


Figure 2. *In situ* measurements of surface potential (mv) as a function of time (min). The arabic numerals in the upper left part of each tracing corresponds to those sample numbers listed in Table 1. The terms "wiped" and "bubbled" are explained in the text. Hand-written pencil and ink notations on the original records were deleted and the traces darkened for clarity. Note that the series beginning with 2A continues for 35 min.

Selected strip chart records are presented in Figure 2. These are photographs of the original records. In the following discussion, "*in situ*" film or measurement refers to the records beginning at zero time before the films were wiped or bubbled. An increase in potential designates an increase in the net dipole moment where the net positive charge is oriented up. Pronounced film patchiness is present in *in situ* (original) films no's. 1, 2, 4 and 6 illustrated in Figure 2. In no. 3 the *in situ* measurements were taken in a very heavy film which apparently was homogeneous in dipolar properties and unbroken in physical structure. This homogeneity was also true for the slick area off La Jolla (no. 5) and within a kelp bed (no. 7) in this same area. One seemingly peculiar nature of this film patchiness is evident from records no. 1, 2 and 4 (night station). In no. 1, the film appears to be isotropic at a minimum V_s value of 300 mv where intrusions of different, higher-potential organic material (or multilayer formation) caused an increase of 245 mv in the surface potential. This situation is essentially reversed in record no. 2 where the high potential film is only occasionally broken to yield low-potential films. Record no. 4 represents an intermediate situation. It is difficult to evaluate such a reversal in patchiness without knowing more about the film thickness and composition, and whether the films present at low V_s values are true monolayers. Surface films can "raft" up on each other leading to layers many hundreds of angströms thick. In this case, V_s values may reach a maximum and eventually decrease as the layers became thicker and the resultant dipolar moments are more randomly oriented.

When the *in situ* film is "removed" with paper towels, the film potential may go down (no's. 2B and 3A) or may remain unchanged (no's. 3 and 4A). When V_s does go down, the resultant film is patchier than the original one, but there is no relationship between the reduction in ΔV_s and the original film characteristics. This may be due to inefficient cleaning techniques in some instances or to very rapid (<10 sec) film formation from subsurface organic matter.

Estimation of film-formation rates from these preliminary measurements are possible only for records 2A, 2B and 2C. This 35-minute continuous record shows that when the *in situ* film ($\Delta V_s = 435$ max) is wiped 4 times with paper towels, ΔV_s is decreased initially to a mean ΔV_s of ~ 125 mv. After standing for 9 min, the potential increases to a mean ΔV_s of ~ 225 mv, an increase of ~ 10 mv min^{-1} . This formation rate is similar to those found in laboratory studies on surface seawater samples (Van Vleet and Williams, 1979). When this same system is then bubbled for 13 min, the mean V_s increases to 250 mv or ~ 2 mv min^{-1} . This increase in potential represents the net change due to bubble transport of surface active material to the surface and concurrent removal of some fraction of this material by bursting bubbles. To attain the original maximum V_s value of 435 mv from the "clean" V_s of 125 mv would require about 20 min standing if these measured rates could be extrapolated. Note that after the bubbling is stopped (record 2C), the film becomes more patchy. There were also indications that extremely rapid (<10 sec) film forma-

tion took place between the time the surface was wiped and the electrode was set in place (record no's. 3 and 4, Figure 2).

Comparison of these results with the earlier two measurements of V_s (Bultman et al., 1963) on lake and coastal-ocean waters shows some rather close similarities considering that the latter measurements were taken from a skiff where wall effects were different than those in this work. The maximum increase of V_s between slick and nonslick areas on the West Virginia Lake was ~ 300 mv, where a 20 min strip chart record of V_s vs. time showed the same general features as record no. 1, Figure 2, this paper. The maximum V_s change was also ~ 300 mv between sea-surface slicks and non-slick areas in the coastal water off San Diego. This latter record, unlike those in Figure 1, showed no fine structure in the slick potentials. The similarity of these lake and coastal seawater V_s results to the surface potentials reported here is best seen from the "max-min" values given in Table 1 where the maximum increase in potential at stations 1, 2, 4 and 6 is 245, 235, 220 and 200 mv, respectively.

TOC and total bacteria measurements on surface films and 10 cm subsurface water samples taken at stations 1, 2 and 3 are shown in Table 2. These results are for the initial *in situ* films plus one measurement at station 3, where the surface had been wiped and then bubbled for 10 min, and are typical of a number of additional measurements of TOC and total bacteria taken at other stations where no surface potentials were measured (this data and many other chemical and microbiological properties of surface films in the Gulf of California will be reported elsewhere). The two conspicuous features of the TOC and total bacteria results (Table 2) are (1) the correlation of TOC and total bacteria with high γ_f values at stations 2 and 3; and (2) the expected increase in TOC and total bacteria in the surface film after bubbling.

At present, V_s measurements are being taken on completely trapped water parcels in the lucite box and on water parcels where the scale of turbulent mixing is empirically reduced by placing polystyrene light-diffusers of varying thickness over the bottom, open-end of the box. These experiments should help differentiate between film-formation processes due to diffusive and turbulent transport of surface-active organic compounds. A free-floating tripod for holding the ^{241}Am and Ag-AgCl electrodes is also being tested in order to avoid the wall effects of the lucite box and electrode platform.

Acknowledgments. We are indebted to D. L. Long for designing and constructing R.V. *Adam*. We also appreciate the assistance of C. C. Price and K. J. Robertson for analytical and logistic help in both field and laboratory work. This research was supported by National Science Foundation Grant OCE77-26178. The paper is USCD 10P20-335.

REFERENCES

- Adam, N. K. 1937. A rapid method for determining the lowering of tension of exposed water surfaces with some observations on the surface tension of the sea and of inland waters. Proc. Royal Soc. Lond., Series B, 122, 134-139.

- 1941. *The Physics and Chemistry of Surfaces*. Oxford University Press, Oxford, 436 pp.
- Armstrong, F. A. J., P. M. Williams, and J. D. H. Strickland. 1966. Photo-oxidation of organic matter in seawater by ultra-violet radiation, analytical and other applications. *Nature*, *211*, 481–483.
- Baier, R. E., D. W. Groupil, S. Perlmutter, and R. King. 1974. Dominant chemical composition of sea-surface films, natural slicks, and foams. *J. Recherches Atmosphériques*, *8*, 571–600.
- Barger, W. R., W. H. Daniel, and W. D. Garrett. 1974. Surface chemical properties of banded sea slicks. *Deep-Sea Res.*, *21*, 83–89.
- Bewig, K. W. 1964. Ionization method of measuring contact potential differences. *Rev. Sci. Instr.*, *35*, 1160–1161.
- Blanchard, D. C., and A. H. Woodcock. 1957. Bubble formation and modification in the sea and its meteorological significance. *Tellus*, *9*, 145–158.
- Bultman, J. D., W. D. Garrett, N. L. Jarvis, and J. B. Romans. 1963. Surface chemistry studies on the Bay of Panama. NRL Memorandum Report 1435, U. S. Naval Research Laboratory, Washington, D.C.
- Davies, J. T., and E. K. Rideal. 1963. *Interfacial Phenomena* (2nd edition). Academic Press, New York, 480 pp.
- Fasching, J. L., R. A. Courant, R. A. Duce, and S. R. Piotrowicz. 1974. A new surface micro-layer sampler utilizing the bubble microtome. *J. Recherches Atmosphériques*, *8*, 649–652.
- Gaines, G. L. 1966. *Insoluble Monolayers at Liquid-Gas Interfaces*. Interscience, New York, 386 pp.
- Garrett, W. D. 1965. Collection of slick-forming materials from the sea surface. *Limnol. Oceanogr.*, *10*, 602–605.
- Jarvis, N. L. 1967. Adsorption of surface-active material at the sea-air interface. *Limnol. Oceanogr.*, *12*, 213–222.
- Jarvis, N. L., W. D. Garrett, M. A. Scheiman, and C. O. Timmons. 1967. Surface chemical characterization of surface active material in seawater. *Limnol. Oceanogr.*, *12*, 88–96.
- Menzel, D. W., and R. F. Vaccaro. 1964. The measurement of dissolved organic and particulate carbon in sea water. *Limnol. Oceanogr.*, *9*, 138–142.
- Van Vleet, E. S., and P. M. Williams. Surface potential and film pressure measurements in seawater systems. Submitted to *Colloids and Surfaces*, November, 1979.
- Zisman, W. A. 1941. The spreading of oils in water. Part III. Spreading pressures and the Gibbs adsorption relation. *J. Chem. Phys.*, *9*, 789–793.