

AD613533

**FILM STUDIES OF SURFACE ACTIVE MATERIAL COLLECTED IN
THE NORTH ATLANTIC.**

NAVAL RESEARCH LAB WASHINGTON DC

JUN 1963

613-533

ABSTRACT

Force/area and surface potential/area isotherms of nine samples of organic surface active materials collected from various positions in the North Atlantic were studied on distilled water (acidified to pH 2.0), and synthetic sea water substrates. Each of the six samples collected under approximately the same conditions were similar in surface activity and surface potential. Three samples, collected under different sea conditions or in areas where contamination was likely to occur, varied from this average.

PROBLEM STATUS

This is an interim report, work on this problem is continuing.

AUTHORIZATION

NRL Prob. 61C02-18B

BuWep Task No. RUDC-4B-000/652-1/F001-99-01

FILM STUDIES OF SURFACE ACTIVE MATERIAL COLLECTED IN THE NORTH ATLANTIC

INTRODUCTION

Surface active material adsorbed at the ocean/air interface can modify many physical properties of the sea surface, such as wave structure, surface temperature and the rate of mixing of surface and subsurface waters. The importance of the adsorbed films in modifying the ocean surface has led this Laboratory to make an extensive study of these materials. Samples of surface organic matter previously obtained from the Bay of Panama have been studied and the results are given in (1). These samples were analyzed by infrared and gas chromatographic techniques, and their surface chemical properties were characterized by measuring their surface viscosity vs. film pressure, surface potential vs. area, and film pressure vs. area isotherms. Each sample was found to contain a mixture of saturated and unsaturated fatty acids 8 to 20 carbon atoms in length, their esters, and possibly some lipids and non-polar hydrocarbons.

The present study is a continuation of the effort to characterize the physical and chemical properties of the adsorbed films and, if possible, to determine their origin. This report describes the force vs. area and surface-potential vs. area characteristics of nine samples of surface organic matter collected at various locations in the North Atlantic area.

EXPERIMENTAL

The samples examined in this report were gathered by W.D. Garrett of this Laboratory. All samples listed in Table I, with the exception of N-4, were collected and treated using the procedure described in (2). Sample N-4 was obtained from a subsurface water sample collected by immersing a 5 gallon polyethylene bottle just beneath the sea surface. All samples with the exception of A-5 were dark brown oily or waxy substances. Sample A-5 contained many small spongy black masses that apparently are not typical of the organic material naturally occurring in the sea.

The infrared analysis of these samples was performed by Dr. R.E. Kagarise of this Laboratory (3). The experimental procedure and a discussion of the manner in which each spectral diagram was interpreted has been discussed by other investigators (1). In the present report each sample displayed strong absorptions in those bands characteristic of CH_2 and CH_3 groups, while varying amounts of COOH and esterified carboxyl groups were indicated. Samples A-1, A-2, A-3 and A-4 appear to have an unusually high ratio of $-\text{CH}_2-$ to carbonyl groups. A-4 was found to have unusually weak absorptivity in the carbonyl group fundamental stretching frequency band, while sample A-5 appeared to be essentially an aliphatic hydrocarbon oil. The evidence for

unsaturation in the carbon chains was inconclusive due to masking by adjacent bands.

Force/area and surface potential/area measurements were made on a Langmuir-Adam type film balance. The film pressure was determined using a commercial Cenco-duNuoy torsion head, while the surface potential measurements were carried out using the vibrating electrode method (4). The film balance and vibrating electrode assembly were enclosed in an aluminum box fitted with clear plastic windows and equipped with automatic controls. The film balance trough was of pyrex glass. Each sample of the so-called "sea-slick" material was studied on two substrates, synthetic sea water prepared according to Federal specifications (5), and distilled water acidified to pH 2.0 with hydrochloric acid. To insure reproducibility, several determinations were made for each sample on each substrate. Readings were normally taken every three minutes, but where conditions warranted (e.g. approach to equilibrium was very slow) the intervals between readings were as long as 30 minutes.

Chloroform was used as spreading solvent for each of the samples. It was re-distilled to remove any non-volatile residue, and was found to be free of film forming material. All measurements were made in a constant temperature room maintained at $20.0 \pm 0.2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity.

RESULTS AND DISCUSSION

The force/area and surface potential/area isotherms of the nine samples are presented in Figures 1-9. Each of the samples studied formed a stable, coherent, non-reversible, liquid-expanded type film on both synthetic sea water and distilled water at pH 2.0. All films were stable to film pressures in excess of 30 dynes/cm, and no lens formation or other disparity of film thickness was observed. Also, there was no evidence of film collapse or buckling during the course of the experiments, even though the calculated film thicknesses indicated that the films were several molecules thick at the higher film pressures.

In attempting to interpret the data presented, one must consider that each of the samples may contain a wide variety of surface active and non-surface active components (1). Many of the shorter chain polar molecules may be quite soluble in the aqueous substrates. Thus as the mixed films of sample material are compressed, certain of the less strongly adsorbed molecules may be displaced from the interface (6-9). The more water soluble compounds will likely move into the substrate, while other film components such as the non-polar hydrocarbon compounds and certain weakly adsorbing polar molecules may, due to their insolubility in water, form duplex films above the strongly adsorbed monolayer. Behavior such as this could explain the large apparent film thicknesses observed at the higher film pressures. As yet however, it has not been determined what portion of the displaced material may dissolve and what portion is capable of forming insoluble duplex films.

The surface potential/area isotherms for each of the films on sea water as well as on acid substrates were found to increase as the films were compressed. The data summarized in Tables I and III show that at 2 dynes/cm the values of ΔV for most of the films fell between 210 and 290 mv, each increasing about 100 mv when compressed to 24 dynes/cm. The recorded surface potentials were generally less on synthetic sea water than on distilled water at pH 2.0, but still not as low as would be expected for closely packed films of fatty acids on a basic substrate. Sanders and Spink (10) and Schulman and Hughes (11) each reported that the ΔV of a fatty acid film is extremely sensitive to pH, particularly in the presence of multivalent cations. The ΔV for stearic acid was found to decrease from about 385 mv on an acid substrate of pH 2.0 to about 50 mv on a 0.001 M CaCl_2 solution at pH 8.0. C.O. Timmons (12) has also shown that oleic acid and triolein each have lower surface potentials on sea water than on acid water, the values for a closely packed monolayer of oleic acid decreasing from about 230 mv at pH 2.0 to 50 mv at pH 8.0 (see Figures 10 and 11).

The fact that the surface potential values measured on sea water are not much lower than those measured on acid substrates indicates that the films contain more than long chain fatty acid molecules. Their high ΔV values could be due to several factors, such as the presence of a large number of adsorbed molecules (e.g. alcohols, ethers, etc.) whose surface potentials are not dependent upon pH. It is also possible that the less strongly adsorbed material that is squeezed out of the film at higher film pressures is contributing to the surface potential, but currently we are not able to evaluate this contribution.

Even though the force/area and surface potential/area isotherms as yet have given little information on the composition of the adsorbed materials, they do show that many of the samples collected from various parts of the ocean have markedly similar surface chemical properties. The averaged data for films A-1, A-2, A-3, A-4, B-1 and B-2 given in Table IV show a deviation in film area between 20 and 25%, while the surface potential values have an average percent deviation of only about 10%. Each of these five samples therefore has roughly the same amount of material remaining adsorbed at the interface at a given film pressure, and shows roughly the same film pressure and surface potential. This would indicate that there is a great deal of uniformity in the material that occurs naturally at the surface of the ocean. It may be possible, therefore, to distinguish such naturally occurring surface organic material from the contamination often associated with the passage of ships.

One surface sample that certainly varied from the preceding five due to the presence of contamination was A-5, which the infrared data showed to contain primarily aliphatic hydrocarbon material. In addition to this hydrocarbon, the unusually high surface potential value of 512 mv at 24 dynes/cm also suggests the presence of different polar groups adsorbed at the interface. Samples N-3 and N-4, which also differed from the previous five samples, did not contain unusually large amounts of aliphatic hydrocarbon, or show the

same high surface potential found for A-5. They were collected near Block Island, close to areas of heavy boat traffic, and it is possible they did contain some contaminating material.

Sample N-3 is of special interest in that it is the only sample of the group collected in the presence of a visible slick, and the only one that gave a film approaching monomolecular dimensions at higher film pressures. At the time this film was collected it was a bright sunny day and the water had been extremely calm for several hours. Under these conditions a near equilibrium situation was probably established, with the less strongly adsorbed materials being replaced at the interface by the more stable film forming molecules. Also, under these calm conditions, any thin film of contaminating material present at the surface would be subject to prolonged oxidation by sunlight, perhaps increasing its surface activity.

CONCLUSION

The force/area and surface potential/area isotherms reported indicated that the naturally occurring surface active material adsorbing at the surface of the open ocean, in the presence of normal wind and wave action, has a certain degree of uniformity. Each of the six samples collected under approximately the same conditions was similar in surface activity and surface potential. The three samples of surface organic material that varied from this average, or general surface chemical behavior, were found to definitely contain contaminating aliphatic hydrocarbons or were collected under different sea conditions in an area where contamination was likely to occur. In comparison, the Bay of Nahama samples (1) generally formed fragile films that collapsed at pressures less than 20 dynes/cm with maximum surface potentials of 0.225 - 0.279 volts.

The infrared and gas chromatographic data available on these materials indicate that the principle polar constituent is the carboxyl group. However, the surface chemical properties of these films, particularly their surface potentials are not what would be expected of long chain unsaturated acids. On the basis of the surface chemical investigations it appears as though these samples, even though they behave in generally the same manner, contain a variety of organic materials varying widely in their surface activity.

TABLE I

Samples of Surface Active Organic Material
Collected At Various Locations in North Atlantic

Sample Number	Sampling Location		Appearance of Surface	Date
A-1	39°N	71°W	no visible slick	21 Aug 62
A-2	"	"	"	"
A-3	"	"	"	22 Aug 62
A-4	"	"	"	"
A-5	"	"	"	"
B-1	56°N	50°W	no visible slick	27 July 62
B-2	56°N	51°W	"	30 July 62
N-3	19 miles So. Block Island		visible slick	26 June 62
N-4	"		no visible slick	26 June 62

TABLE II

Summary of Film Properties of Surface Active Organic
Material Collected from the North Atlantic
on Synthetic Sea Water

Sample	Film Pressure (2 dynes/cm)			Film Pressure (24 dynes/cm)		
	Area (m^2/mgm)	Film Thickness ($\text{\AA}$)	Surface Potential (mv)	Area (m^2/mgm)	Film Thickness ($\text{\AA}$)	Surface Potential (mv)
A-1	0.139	75	222	0.060	175	310
A-2	0.207	50	216	0.065	160	333
A-3	0.108	96	241	0.036	290	367
A-4	0.114	91	210	0.047	223	-
A-5	0.289	35	382	0.098	106	512
B-1	0.195	52	235	0.088	120	312
B-2	0.095	110	157	0.041	251	231
N-3	0.810	13	251	0.300	27	308
N-4	0.291	35	271	0.115	87	390

TABLE III

Summary of Film Properties of Surface Active
Organic Material from North Atlantic on
Acid Water (pH 2.0)

Sample	Film Pressure (2 dynes/cm)			Film Pressure (24 dynes/cm)		
	Area (m^2/mgm)	Film Thickness ($\text{\AA}$)	Surface Potential (mv)	Area (m^2/mgm)	Film Thickness ($\text{\AA}$)	Surface Potential (mv)
A-1	0.134	78	251	0.044	239	345
A-2	0.197	53	225	0.067	157	338
A-3	0.113	93	251	0.035	301	346
A-4	0.107	98	231	0.043	245	-
A-5	0.326	32	453	0.095	111	634
B-1	0.175	60	245	0.073	144	330
B-2	0.095	111	232	0.037	285	330
N-3	0.793	13	285	0.281	37	352
N-4	0.349	30	291	0.086	122	-

TABLE IV

Average Film Properties of Samples A-1, A-2, A-3, A-4, B-1 and B-2 on Synthetic Sea Water

Film Pressure (dynes/cm)	Surface Active Material from Sea				Oleic Acid	
	Film Area (m^2/mgm)	Film Height ($\text{\AA}$)	Surface Potential (mv)	Film Area (m^2/mgm)	Film Height ($\text{\AA}$)	Surface Potential (mv)
2	$0.143 \pm .037$	79 ± 20	214 ± 20	1.310	8	80
24	$0.056 \pm .015$	205 ± 52	311 ± 32	0.642	16.0	45
30	$0.043 \pm .009$	260 ± 57	---	0.581	18.0	45

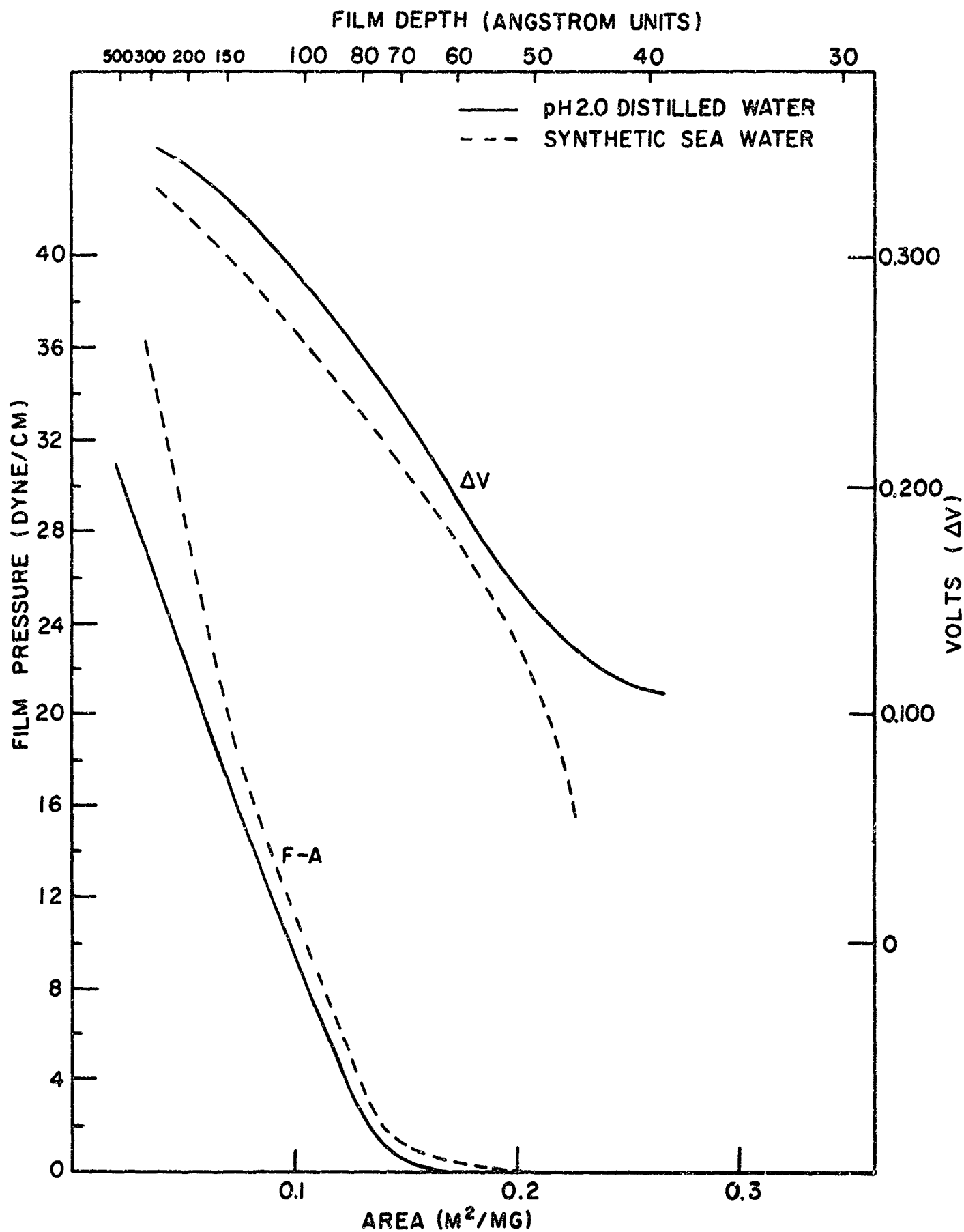


Figure 1 - Force/area and surface potential/area isotherms for sample A-1

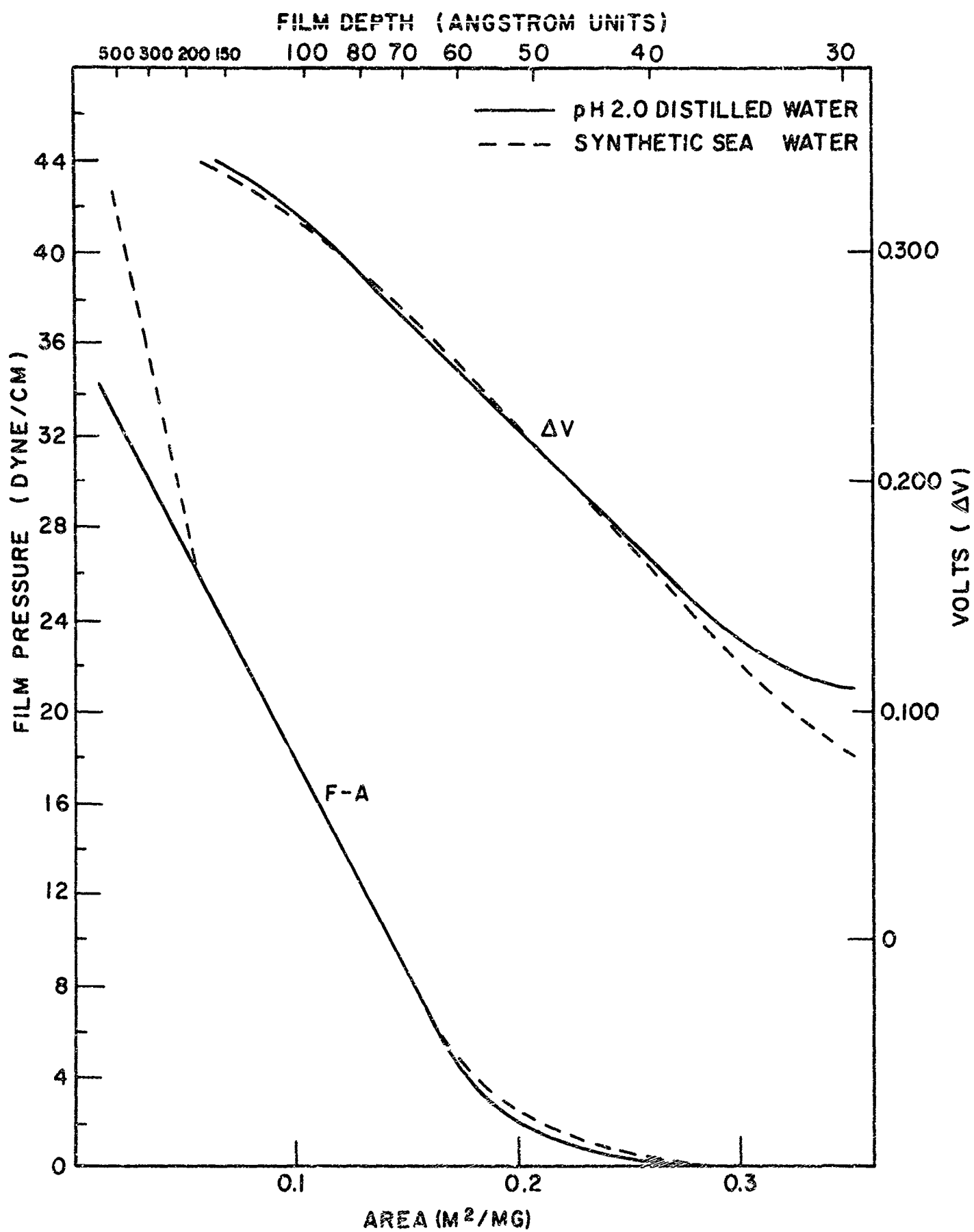


Figure 2 - Force/area and surface potential/area isotherms for sample A-2

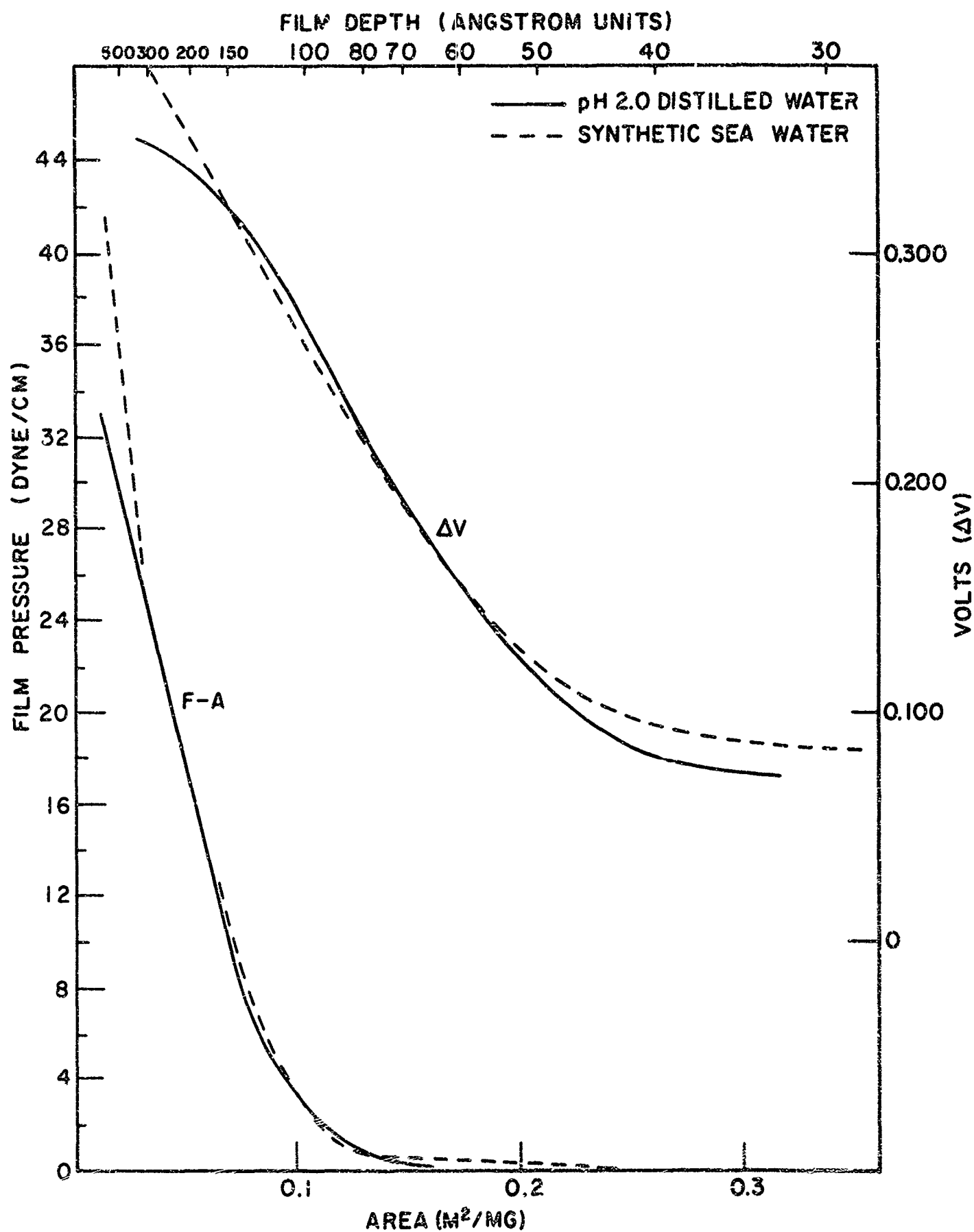


Figure 3 - Force/area and surface potential/area isotherms for sample A-3

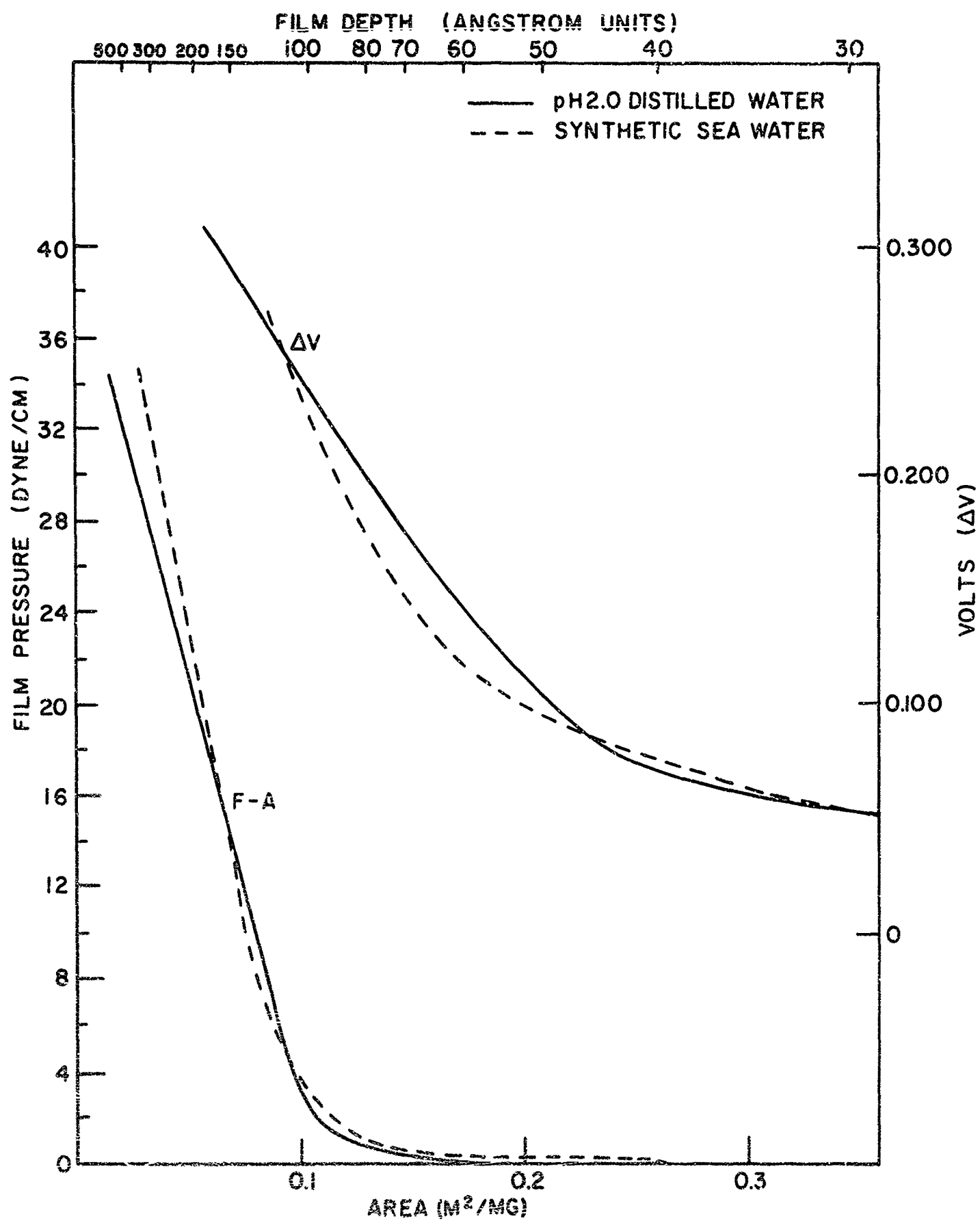


Figure 4 - Force/area and surface potential/area isotherms for sample A-4

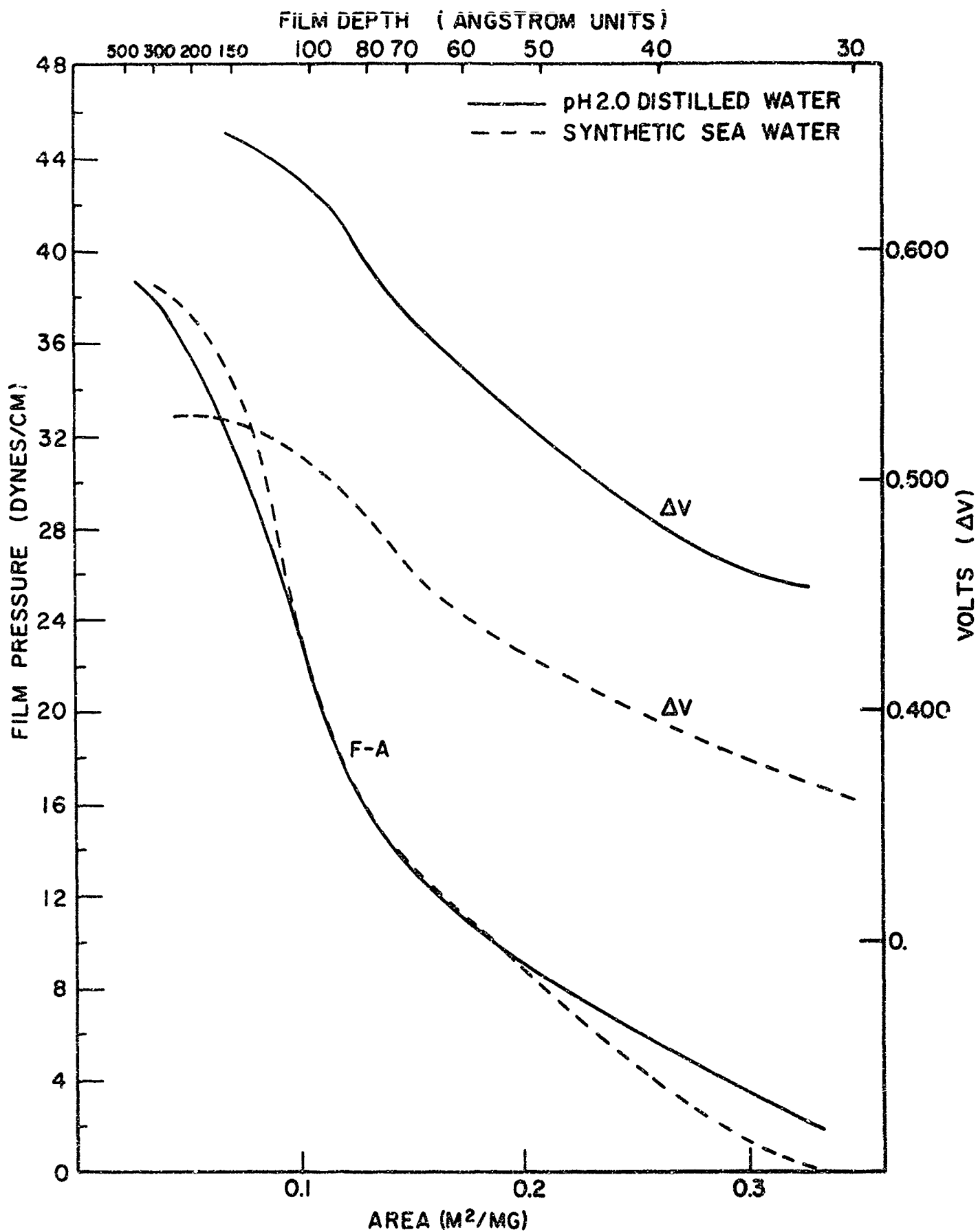


Figure 5 - Force/area and surface potential/area isotherms for sample A-5

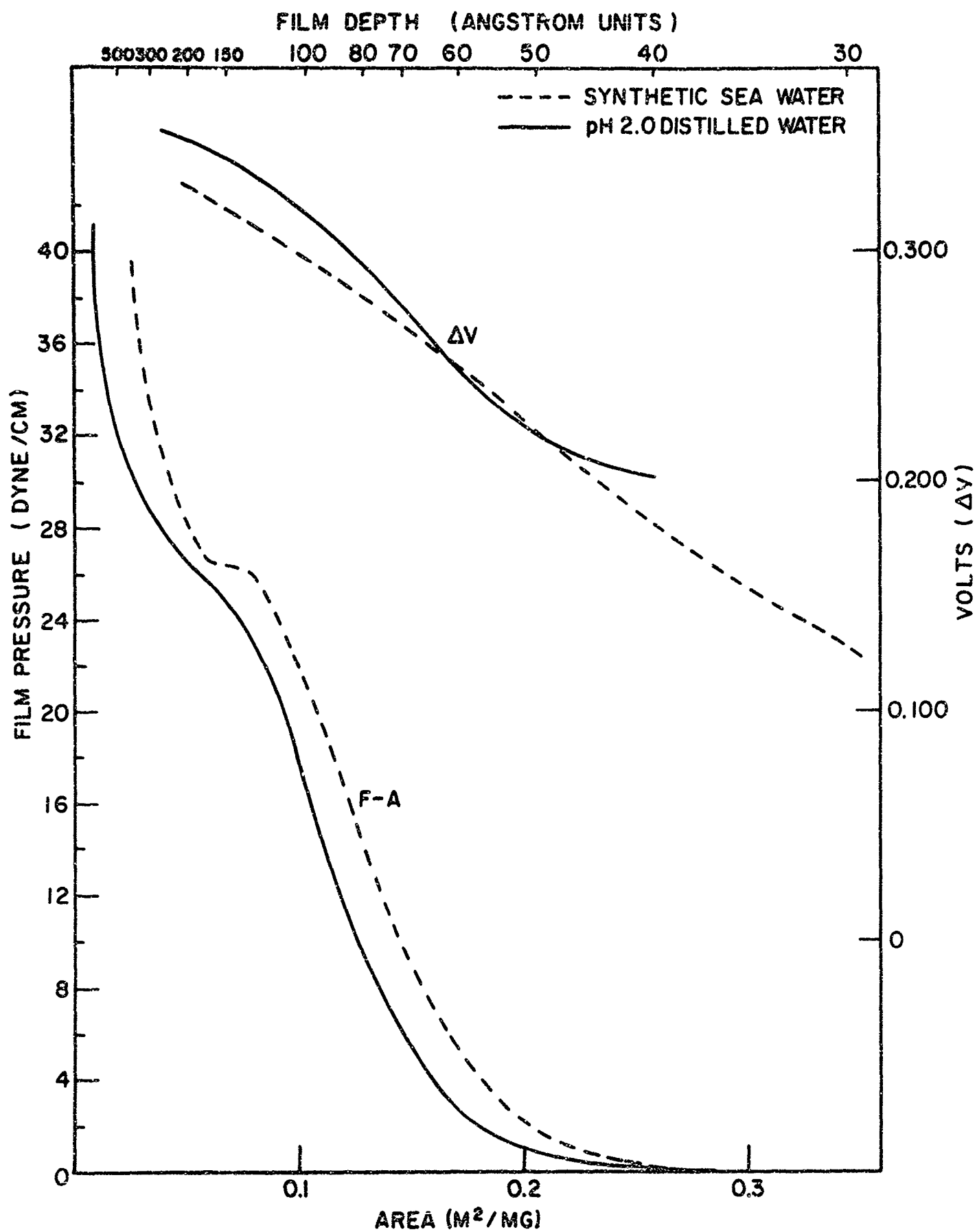


Figure 6 - Force/area and surface potential/area isotherms for sample B-1

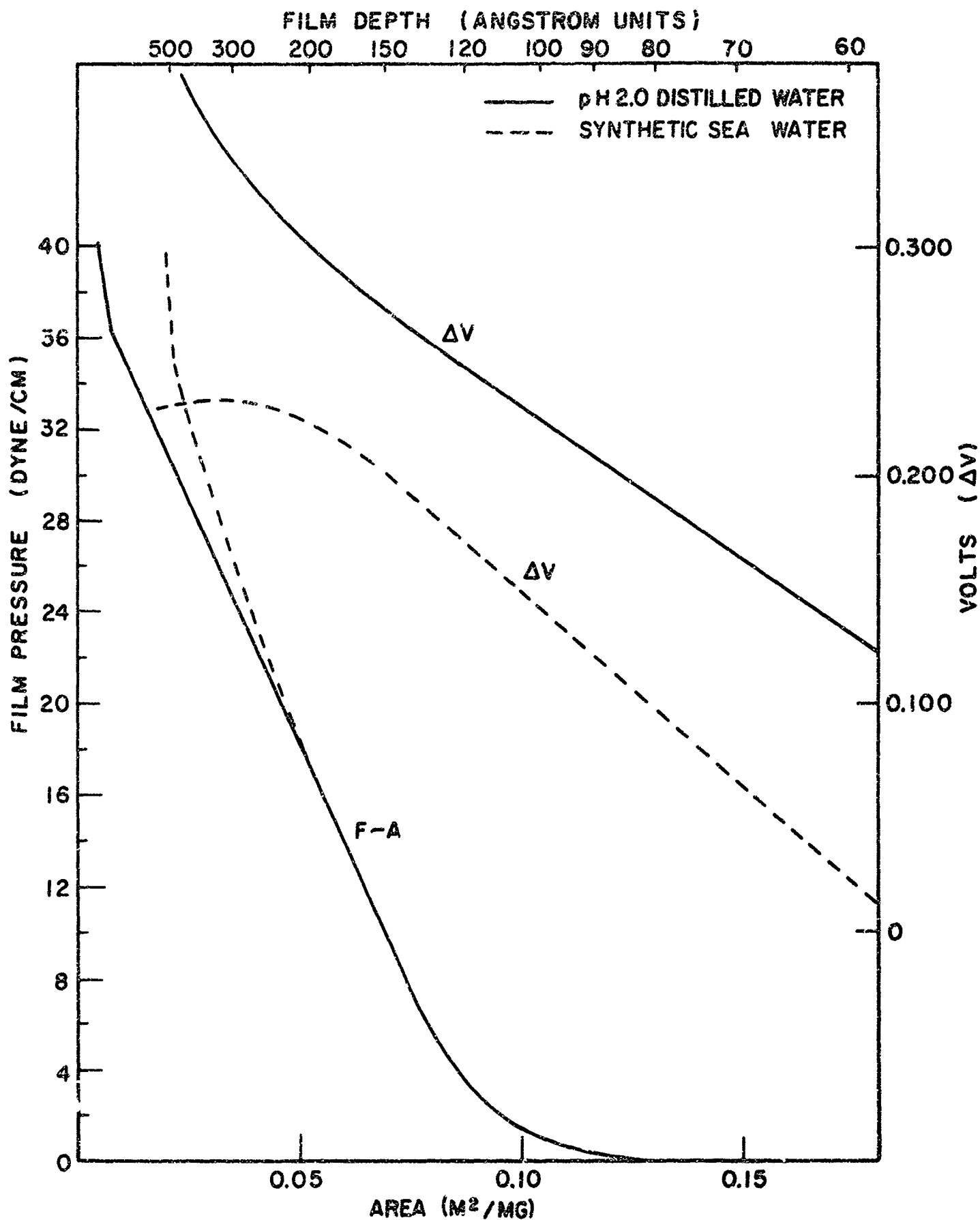


Figure 7 - Force/area and surface potential/area isotherms for sample B-2

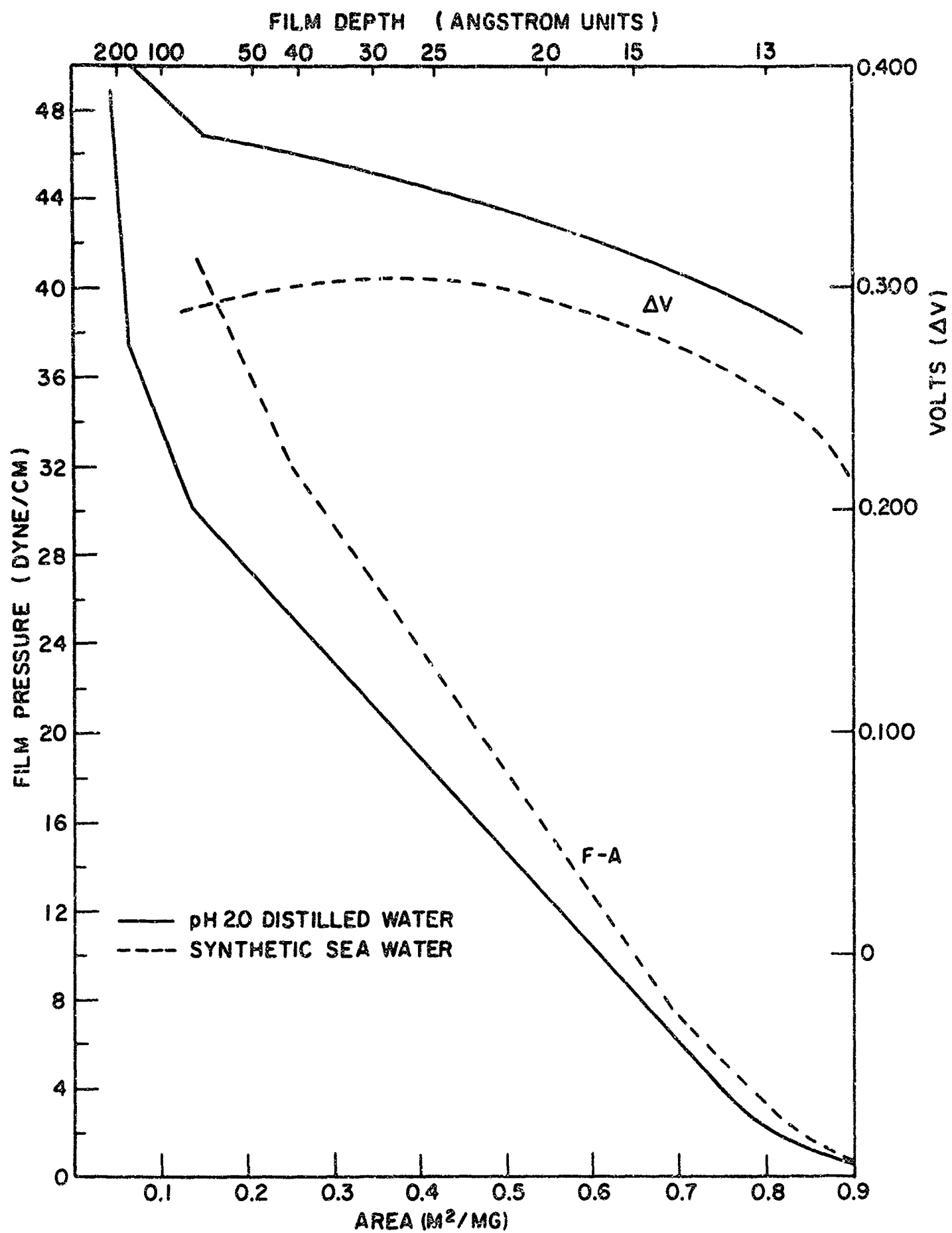


Figure 8 - Force/area and surface potential/area isotherms for sample N-3

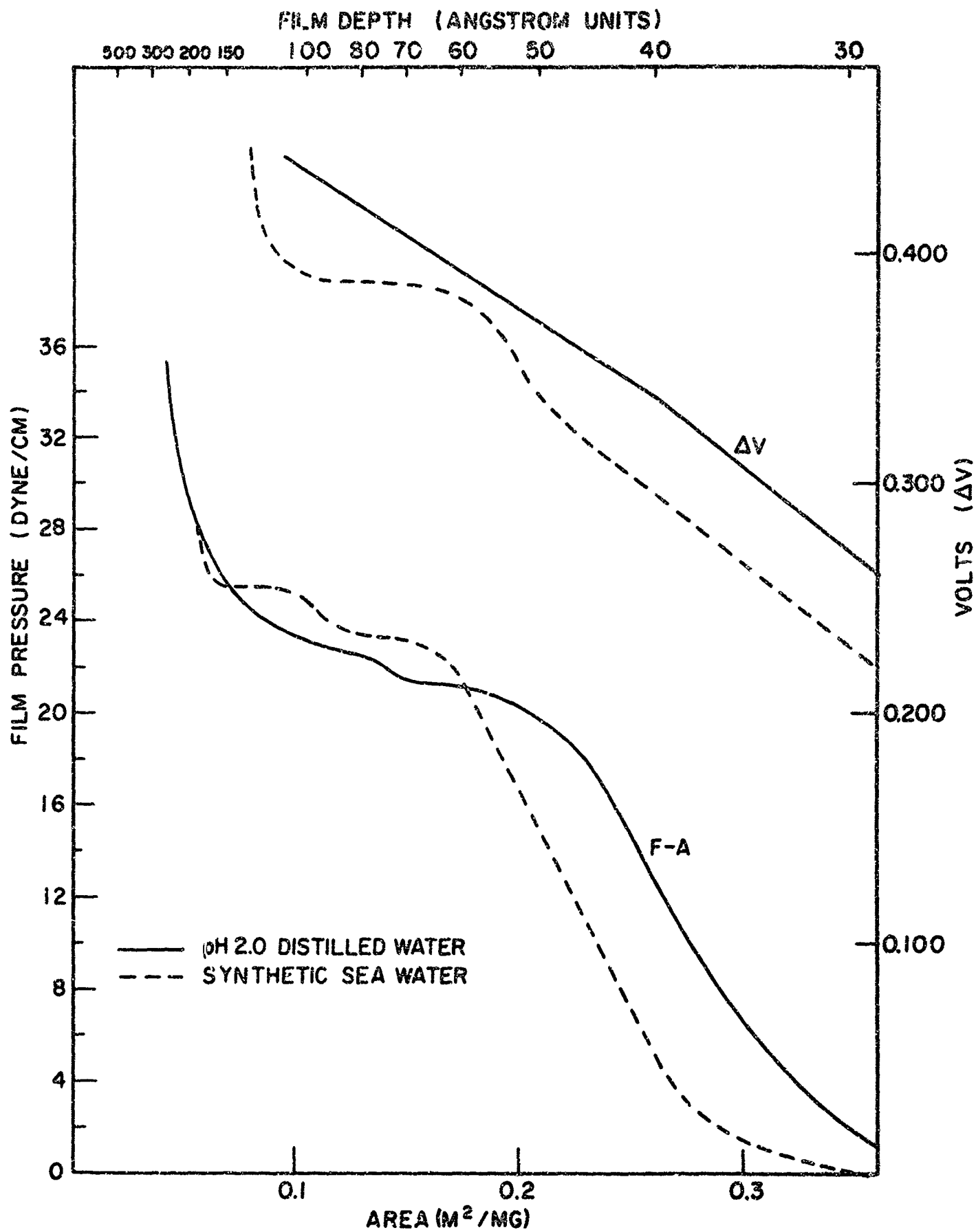


Figure 9 - Force/area and surface potential/area isotherms for sample N-4

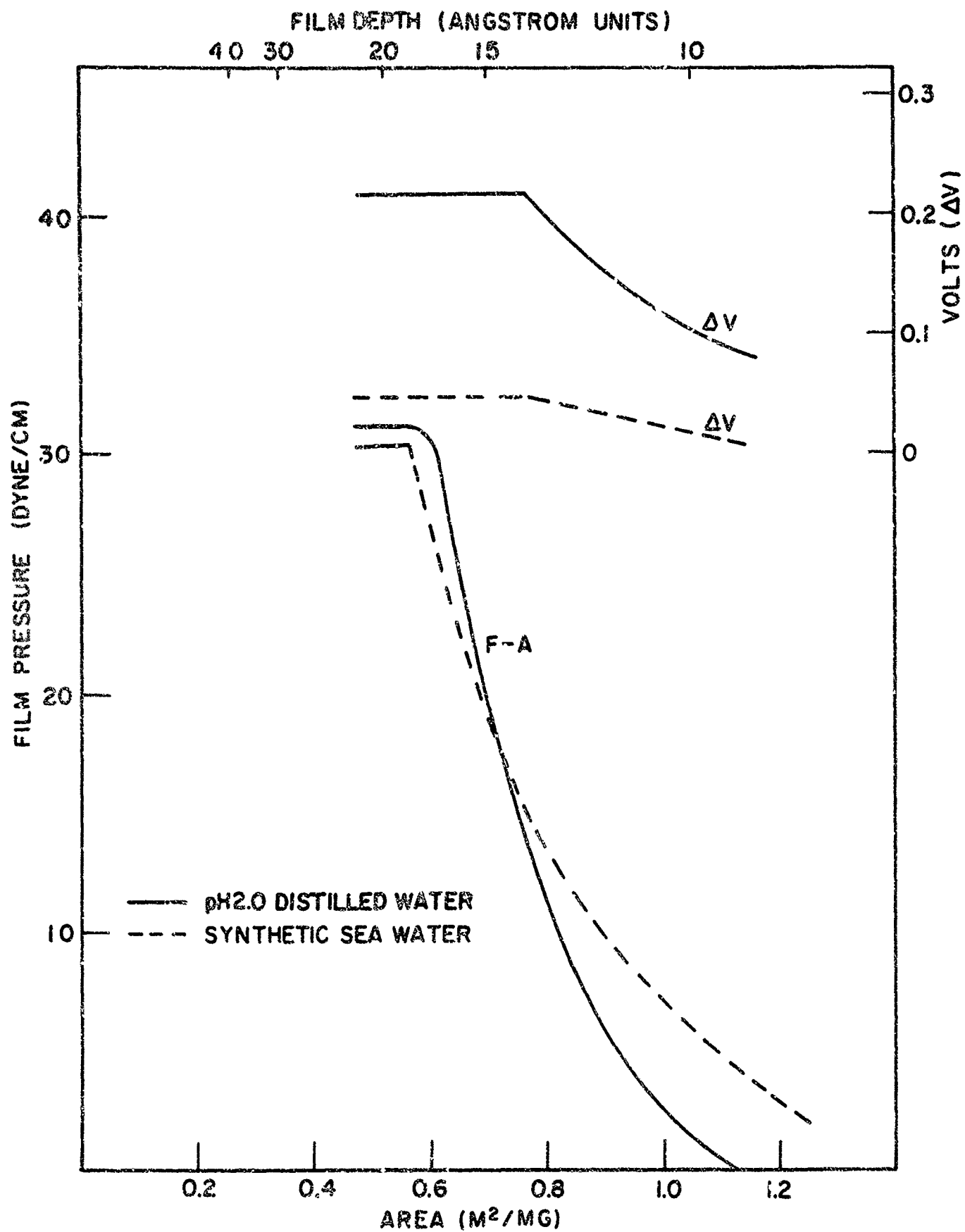


Figure 10 - Force/area and surface potential/area isotherms for Oleic Acid

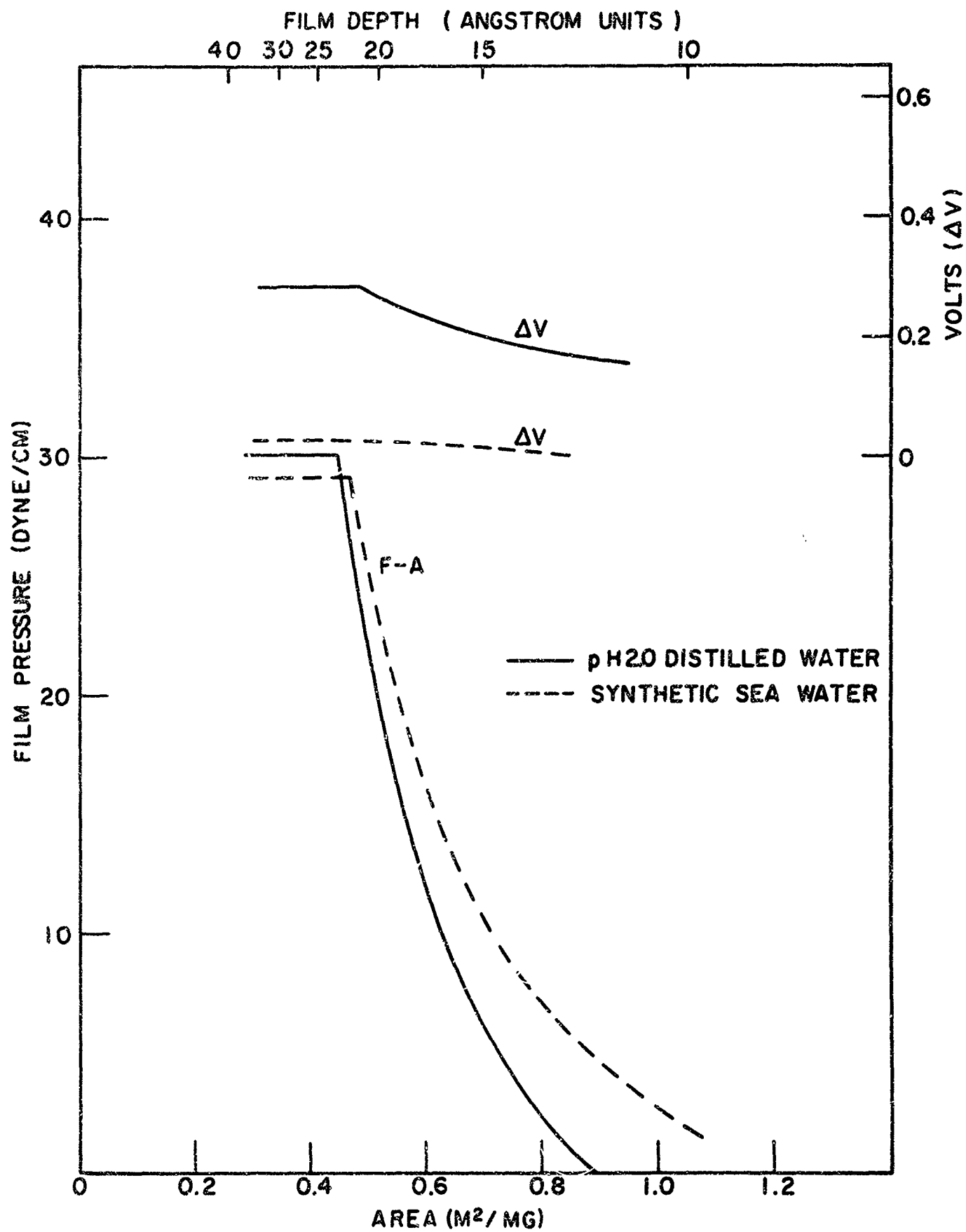


Figure 11 - Force/area and surface potential/area isotherms for Triolein

Bibliography

1. Garrett, W.D., Kagarise, R.E., Timmons, C.O., and Jarvis, N.L., "Constitution and Surface Chemical Properties of Sea Slicks", NRL Report 5925, to be published
2. Garrett, W.D., "Collection of Slick-Forming Materials from the Sea", NRL Report 5761, Mar. 5, 1962
3. NRL Memorandum, Code 6110 to Code 6170, 6110-257:REK:ht, 25 Sept. 1962
4. Zisman, W.A., Rev. Sci. Instr. 3:369 (1932)
5. Federal Specification VV-L-791e, "Lubricants, Liquid Fuels and Related Products; Methods of Inspection, Sampling, and Testing", Method 4011.2, 21 May 1953
6. Schulman, J.H., and Hughes, A.H., Biochem. J. 29:1243 (1935)
7. Florence, R.T., and Harkins, W.D., J.Chem.Phys. 6:856 (1938)
8. Harkins, W.D., and Myers, R.J., J.Am.Chem.Soc., 58:1817 (1936)
J.Phys.Chem., 40:959 (1936)
9. Fowkes, F.M., Myers, R.J., and Harkins, W.D., J.Am.Chem.Soc., 59:593 (1937)
10. Sanders, J.V., and Spink, J.A., Nature 175:644 (1955)
11. Schulman, J.H., and Hughes, A.H., Proc.Royal Soc. (London) 138.430 (1932)
12. Timmons, C.O., private communication

BLANK PAGE

SHEET

1 OF 1

END

Reprinted from

DEEP-SEA RESEARCH
and Oceanographic Abstracts

COPY	Gr	
HARD COPY	\$.	
MICROFICHE	\$.	



PERGAMON PRESS

OXFORD • LONDON • NEW YORK • PARIS

Copies available
only to 120 users

ARCHIVE COPY