

The dynamic surface tension of sea water as a measure of pollution

by

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The dynamic surface tension of a sea water sample, measured by the Wilhelmy plate technique in a Langmuir type trough, yields a measure of the interfacial energy. It is known that the energy barrier for the transport of gases across the sea water/air interface depends strongly on the constitution of surface films.

The instrumental device for the surface tension measurements is commercially available. The one used in this research has been the Dynamic Surface Tension Accessory to the Cahn Electrobalance RG (Cahn Instruments, Ventron Corp. Palo Alto, Calif.). The device consists of the Wilhelmy platinum plate used in the equilibrium mode in a PTFE lined trough, filled with the sample of sea water under investigation. Two motor-driven slides are moving along the surface compressing and expanding the surface with the surface active layer in which the Wilhelmy plate is partially immersed. In this sense the electrobalance records the change in the surface tension produced by surface compression and decompression cycling.

Results were obtained for the surface pressure of sea water samples (collected by means of the Garrett screen) with addition of oleic acid. The dynamic behavior of sea water samples with additions of various concentration of oleic acid below and above monolayer formation is shown in Fig. 1.

The figure shows the surface tension of sea water samples with additions of increasing amounts of oleic acid (cis-9-octadecenoic acid). The concentration of oleic acid is expressed in number of molecules per unit surface, assuming that oleic acid is insoluble and that all the molecules added are present in the surface film. The point of this presentation of the amount of oleic acid v.s. the dynamic surface tension curve is that one can measure an unknown sample and simulate conditions in the laboratory comparison sample, until the two are as closely as possible matched. It should be noted that the area inside the curve has the dimension of energy. For a sample of sea water, collected from the surface in a frequented resort port the dynamic surface tension — area curves are shown in Fig. 2.

The curve at the top of Fig. 2. is a real sample taken from an unpolluted part of the sea near a resort town. The curve at the bottom is the sample of sea water taken in the port, very close to a sewage outlet. The curve in the center is the top sample with additions of oleic acid. The matching in this instance has been done as closely as possible to the shape of the curve and not to the loop surface area.

Other types of surfactants, like the soluble nonionic polyethyleneglycol (PEG-4000), can also be used for calibration or comparison purposes. It is essential to simulate real conditions and to investigate whether the contaminated sample shows condensed, expanded, or soluble surface film type of behaviour (see reference 1.).

The final result of the presentation is a suggestion that surface pollution of water should be expressed in terms of a concentration of typical surfactants rather than in pure chemical analysis of the species present.

Reference

- [1] DAVIES J.T. & RIDEAL E.K., *Interfacial Phenomena*, Academic Press, New York 1961. **5**, pp. 217-281.

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Rapp. Comm. int. Mer Médit., **23**, 7, pp. 39-40, 2 figs (1976).

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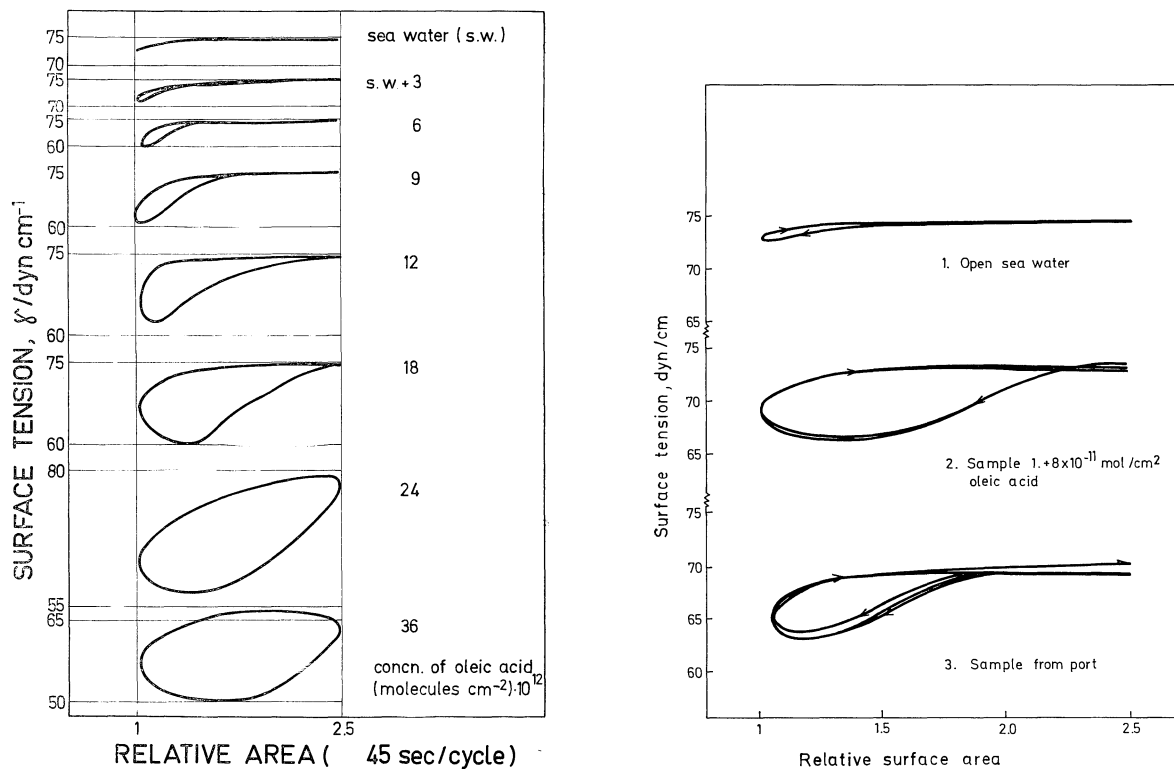


FIG. 1. — The dynamic surface tension of sea water samples with various additions of oleic acid. Measurements are done in the Wilhelmy plate method with an electrobalance recording the compression-expansion phenomena for a relative area 1 : 2.5 at 45 sec/cycle.

FIG. 2. — Simulation of water pollution level with oleic acid. Sample of clean sea water (curve 1.) is treated with oleic acid (curve 2.), until the shape of the curve resembles polluted sea water (curve 3.). Dynamic surface tension measurement with a Wilhelmy plate, relative surface area displacement 1 : 2.5 at 45 sec/cycle.

Discussion

Dr. Bozena Cosovic : Which type of surface behavior you expect in the case of a mixture of different substances?

Answer : In principle the method can approximate any behavior. The point is that there is no way of predicting by how many of several thousands of possible substances pollution might have occurred. Therefore we suggest just two specific substances. One is oleic acid, which gives the so called "expanded" type of surface film; the other is polyethyleneglycol (PEG-4000) which gives the most representative type of "soluble" films. Both calibration substances are easily accessible and can be used without difficulties. One just prepares a standard solution of this substance in a ethanol-water mixture and titrates the surface. Almost any type of observed behavior can be simulated.

Dr. Vera Zutic : Can this method of measuring pollution be used to differentiate between naturally occurring lipid films and oil films?

Answer : Many lipid films produce "condensed" type surface films, oil and their fractions mostly of the "expanded" type (cf. reference 1.). There is the possibility of estimating which one is present, at least in principle. But this is neither our aim, nor the purpose of the method. We just suggest a quantitative comparison method relating to the surface energetics, and not to the analytical aspects.

Dr. Michael Bernhard : How do you correlate your measurements with gas exchange?

Answer : The gas exchange measurements have not been done, as this is another project in itself. The surface tension measurements are related to the total interfacial energy. Changes in this are expected to affect any gas exchange where the surface film is the site of the rate determining step of the exchange kinetics.