ELECTROCHEMICAL CHARACTERIZATION OF UNSATURATED LIPID DISPERSIONS IN MARINE AQUEOUS SAMPLES

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Summary. Fluid surface-active aggregates have been detected and characterized in North Adriatic aqueous samples and compared with artificial dispersions of unsaturated fatty acids and phytoplankton cultures using a direct electrochemical method. The geochemical implications are discussed.

Resummé. Les agrégats fluides de matière organique tensioactive ont été détectés et caractérisés dans les échantillons aqueux dans l'Adriatique du Nord utilisant une méthode électrochimique directe. On discute sur les sources naturelles et implications géochimiques.

In natural waters hydrophobic compounds commonly exist in a micellar or colloid accomodated state rather than as true molecular solutes[1]. It is well known that the degree of aggregation influences transport properties and interactions of hydrophobic organic matter with surfaces and solutes in marine environment. However, fluidity of aggregates that affects dramatically the rate of interactions at interfaces[2], has not been adequately taken into account.

The electrochemical method of polarographic maximum, with a high sensitivity based on the interfacial instability and catalytic effects at the mercury electrode/seawater interface[3], allows direct characterization of coalescence and transformation of single agglomerates of fluid surfactants (such as unsaturated lipids) at interfaces, that take place in the time scale 10 ms – 1 s.

Dispersions of unsaturated lipids (e.g. oleic and linolic acids and their esters) produce irregular oscillations in polarograms owing to random collisions of aggregates of variable size with the adsorbed layer at the electrode. By recording the current-time curves it is possible, in principle, to evaluate the distribution and aggregation number of fluid aggregates and the relaxation time of their reorganization into the adsorbed layer at the interface. Measurable effects are obtained for dispersions of 50 µg–100 mg total unsaturated lipids per liter. However,

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highly unsaturated fatty acids, as linolenic acid, behave as solutes be-
cause of their higher solubility and mobility of alkyl chains.

The presence of adsorbable solutes, such as refractive dissólved organic
matter, decreases the effect of heterodispersions owing to the competi-
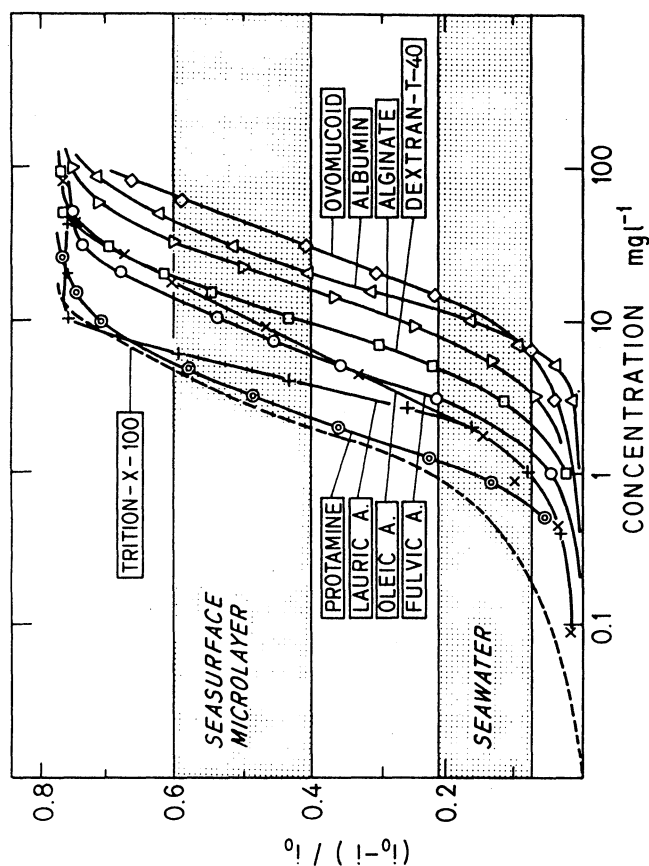tive adsorption at the electrode. Solubilization of lipid aggregates

Fig. 1   Dependence of supression of the polarographic
maximum (10^{-3} M Hg(II) added to the artificial
water, measured at -o.3 V/SCE) on the concentration
of various model surfactants. Typical range of
responses for natural seawater and sea surface
microlayer are indicated.

should be also considered[4].

Response of the typical natural sea surface microlayer sample can be si-
mulated by the artificial mixtures of oleic acid and humic material
(Cauwet) in the organic-free seawater.

Oleic acid-like aggregates were occasionally detected in sea surface
microlayer samples as well as in subsurface waters of the North Adriatic,

which is characterized by a high primary productivity and frequent phytoplankton blooms. Natural sources of fluid surfactant dispersions seem to be predominantly phytoplankton. The release of vesicles with a high content of unsaturated lipids was found in laboratory cultures of microflagellates (e.g. Dunaliella tertiolecta, Cryptomonas sp., Ochromonas danica). The measured response was equivalent to the dispersions of up to 50 mg oleic acid per liter seawater. The effect was much less significant in diatom cultures.

These findings have important implications in the transport and scavenging of hydrophobic natural organic matter and pollutants in estuaries and coastal areas, as well as in the migration and accumulation of the petroleum source material. Moreover, the concept of surfactant activity of seawater[5,6] should be reconsidered and related to the adsorbable organic matter rather than to the dissolved one.

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"Electrochemical characterization of unsaturated lipid
  dispersion in marine aqueous samples"

Paper presented by V. Žutić (Yugoslavia)

Discussion

M. Branica: Can you discuss on the current response
                     vs. concentration and the type of SAS
                     present in natural and polluted seawater
                     samples?

V. Žutić: The best answer to your question can be
given by the diagram (Fig. 1) where the
supression of polarographic maximum is
plotted against concentration of various
model surfactants. An artificial mixture
of humics and oleic acid best simulates
the response of natural seawater.
The form of the current vs. concentration
curves for different surface active
molecules depends not only on their
intrinsic adsorbability but also on the
rate of their transport to the interface
In the majority of natural seawater samples
concentration of surface active materials
is low, and as the time of measurement is
2 sec, the extent of adsorption is determin-
ed by the rate of mass transport to the
interface. The diffusion coefficient, i.e.
the size of surface active molecules, is
the decisive factor.

H.W. Nürnberg: Why did you not reach a full coverage?
The measurements strongly reflect the
influence of the diffusion rate. This masks
to a certain extent the surface activity
of the studied substances. It turns out
that within 2 s life time of the drop the
smaller less surface active substances
have a relatively larger effect than the
more surface active larger polymeric
molecules which have a lower diffusion rate.

V. Žutić: You have perfectly explained what happens
to the mercury drop during the measurement
at the time scale of 2 sec.
As at the electrode/seawater interface,

adsorption of surface active molecules
at natural interfaces such as particle/sea-
water is mostly transport controlled, since
the concentration of surfactants is low
and the contact time during the passage
through the water column is relatively short.
In this respect the dropping mercury
electrode represents a convenient model to
study particle/surfactant interaction in
natural waters.

P. Valenta: Using of the i-t curves of the reduction
of Hg could be also used for the estimation
of the diffusion coefficient of substances
from the time interval up to the onset of
the capacity current. Of course, in a
mixture of surfactants the use of this
method will be limited.

V. Žutić: This is a very important point. The method we
presented could be used, in principle, even
to determine the diffusion coefficients of
fluid aggregates in a heterodisperssion, if
their distribution were known.
For a mixture of surface active molecules of
a different molecular weight, but of a similar
type, such as the most likely the refractive
organic matter in the ocean is, this approach
can still be used and a value of the mean dif-
fusion coefficients $\overline{D}$ could be obtained
experimentally. Our preliminary estimate indicate
that this value for the adsorbable organic
matter in seawater is close to $\overline{D} \cong 4 \times 10^{-6}$ $cm^2 s^{-1}$.