The Microcalorimetric measurements of interaction of sediments with Sea water

by

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The interaction of solid surfaces of sediments with the medium of sea water and with major pollutants present in it can be successfully studied by the microcalorimetric techniques.

In this technique a sample of solid dispersed material, like a sediment sample, is evacuated in a small bulb under controlled vacuum and temperature. The small bulb is sealed off after a predetermined time, and then brought into the cell of the microcalorimetric unit, in which a carefully measured amount of a liquid is contained (sea water, sea water with oil, detergents or any other substance of interest). After temperature equilibration the sample bulb is broken in such a way, that the sediment sample is instantaneously coming into contact with the liquid. A heat effect usually an endothermic one, is measured by the sensitive thermistor. If the surface area of the sample has been determined beforehand, by e.g. nitrogen adsorption (BET methodology), one can calculate the specific heat of immersion per unit surface area.

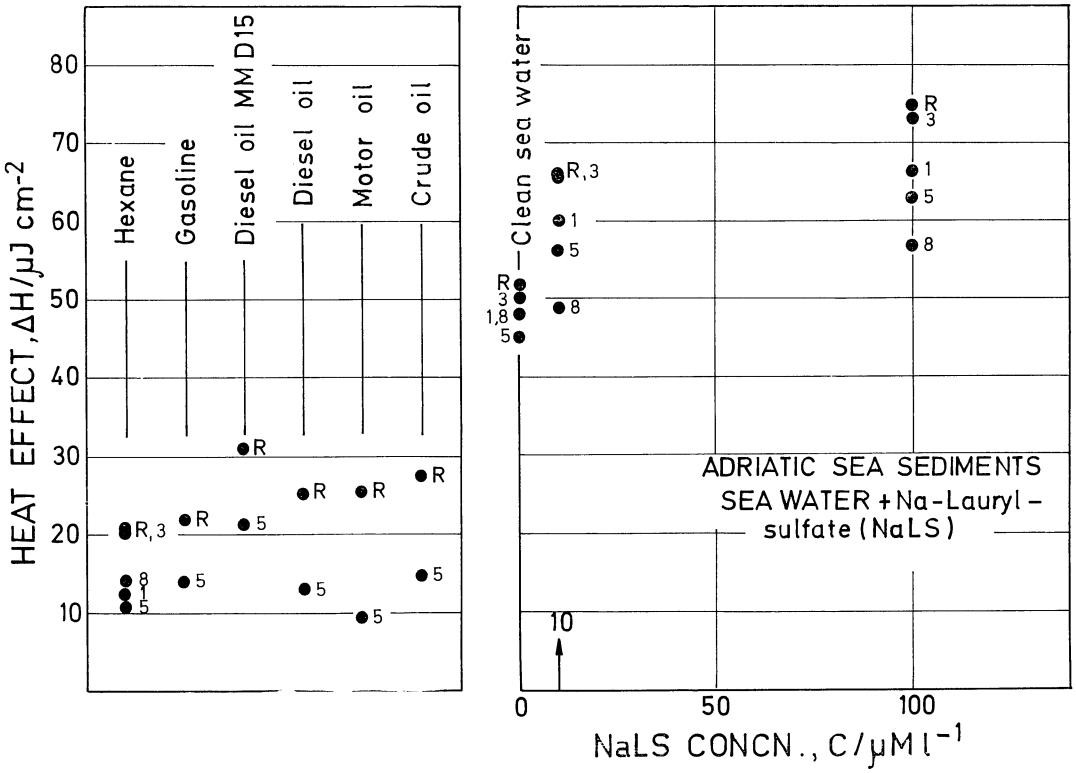

FIG. 1. — The heat-of-immersion of sediments into petroleum hydrocarbons (left hand part of the figure), and into sea water, and sea water with additions of a detergent (sodium lauryl sulfate).

Rapp. Comm. int. Mer Médit., **23**, 7, pp. 65-66, 1 fig. (1976).

The technique, as developed, is sensitive down to 120 microjoules, and thus is suitable for use with sediments, of specific surface areas between 1 and 20 m^2/g, and of specific energies of interaction in excess of 10 microjoules/cm^2.

The results show that for some typical Adriatic sea sediments the energy of interaction is dependent on the carbonate content. Also the organic coating of the sediments increases significantly the energy of interaction. The pH dependence of the interaction is quite large in some examples, indicating the profound influence of acid dumping on adsorption properties of sediments. Addition of an anionic detergent, sodium laurylsulfate (NaLS), increases the interaction energy with respect to pure sea water.

Fig. 1. shows summarily the measured heats-of-immersion of a variety of Adriatic sea sediments into sea water, and into sea water with the addition of a detergent. From these data it follows, that the petroleum hydrocarbons will be adsorbed with considerably lesser energy than water, or water with detergents. These data should be considered in using sediments for oil clean-up.

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Discussion

Q. : ***Dr. Charles Murray :*** Work carried out at the Monaco Laboratory on the interaction of heavy metals with freshwater sediments and sewage has shown, that adsorption may be increased in the presence of organic coatings on the sediments. On desorption into sea water, certain elements showed an increased ability to desorb. Could you, in fact, explain these results on the basis of your experimental work.

A. : The work presented here relates mostly to macro components of the sea water medium, and to macropollutants. For those, the energetics of adsorption is well understood by measuring the heats-of-immersion. But for microcomponents, a much finer energetics, that of metal-organic ligand complex formation, is all important. For such studies a different approach is needed. The heats-of-immersion technique is essentially too crude to allow any insight into the proces of trace metal adsorption-desorption equilibria. But the adsorption of organic coatings could be studied. Provided of course that it has occured by adsorption from sea water, and not in the digestive tracts of some worms.

Q. : ***Dr. Michael Bernhard :*** You should take the degradation of oil by microorganism into consideration.

A. : Certainly. But some petroleum hydrocarbons, specifically some olefinic and aromatic are quite resistant to microbial attack (the microbes do not like them). The point of our discussion is, however, only to see whether or not oil will adsorb at the sediment particles and remain there. A weak interaction is the reason for spreading of petroleum hydrocarbons along the sea floor to unexpected distances. And here we do provide an answer why is this the case.