ON INTERACTION OF CADMIUM(II) WITH SURFACTANTS.
MODEL STUDIES AT ELECTRODE/SEA WATER INTERFACE.

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Summary

The inhibition of the electrode reaction of Cd(II) in the presence of sur-factants was studied by differential pulse polarography.

Résumé

On a étudié l'inhibition de la réaction électrode du Cd(II) en présence des surfactants par la polarographie impulsionelle.

Surfactants, both natural and pollutants, adsorb and accumulate at natural interfaces (seawater boundaries with atmosphere, sediment and dispersed particulate material and biota). The study of adsorption phenomena and mass and charge transfer processes at charged electrodes, opens new pos-siblities for the simulation of interfacial phenomena and processes at natural phase boundaries (1,2).

The effect of adsorbed surfactants on the electrode processes of cadmium was studied by differential pulse polarography at the hanging mercury drop electrode. The kinetic parameters, the rate constant k_s and the transfer coefficient α of the electrode reaction of cadmium were estimated from the shape and the height of the corresponding differential pulse polarograms, using theoretical curves obtained by digital simulation (3).

Inhibition effects of surfactants present in natural and polluted seawater, phytoplankton culture media and effluents containing different types and concentrations of surfactants, have been investigated. It was found that effluents which contain predominantly synthetic compounds show considerable influence upon the electrode reaction of cadmium, while the effect of sur-factant constituents of seawater and phytoplankton media, mainly biogenic compounds, was practically neglegible. Results are given in Table 1.

References

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   tants Studied by Differential Pulse Polarography. Cadmium(II) in
   Seawater in the Presence of Triton-X-100. J. Electroanal. Chem.,
   137 pp., 279-292.

Table 1.

The influence of surfactants present in:
a) seawater samples taken at pollution sources,
b) phytoplankton culture media, and
c) effluents from plastics factory, on kinetic parameters of electroche-
   mical reduction of 10^{-4} mol dm^{-3} cadmium(II). In sodium chloride
   0.55 mol dm^{-3} without surfactants kinetic parameters for cadmium are:
   $k_s \geqslant 1.12 \times 10^{-1}$ cm s^{-1},　$\alpha = 0.5$.

a) seawater samples taken at pollution sources

Sample	Surfactants eqv.T-X-100 (mg dm^{-3})	Kinetic parameters of electrode reaction	
		α	k_s (cm s^{-1})
Harbour	0.84	0.5	7.8×10^{-2}
Fish factory	2	0.5	4.5×10^{-2}
Surface film taken in front of fish factory	3.3	0.5	1.12×10^{-1}
Effluents outlet	0.6	0.5	2.5×10^{-2}

b) phytoplankton culture media ($\sim 10^6$ cells ml^{-1})

Dunaliella tertiolecta	0.55	0.5	3.4×10^{-2}
Thalassiosira pseudonana	0.14	0.5	5×10^{-2}
Chlorella	0.39	0.5	1.6×10^{-2}
Chryptomonas Sp.	11.5		1.7×10^{-2}

c) effluents from plastics factory

Emulsion polimerization	31		$2-3 \times 10^{-3}$
Phtalate esters	> 1000	0.4-0.5	5×10^{-3}

Kozarac, Z., Ćosović, B.
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Paper presented by Z. Kozarac (Yugoslavia)

Discussion

I. Vukadin: What is the thickness of your surface film
                     and how did you take it?

Z. Kozarac: Surface film samples were taken by Garrett's
                     sampler, a 16 mesh stainless steel screen
                     (85 cm x 7o cm). The sampler collects the
                     top 1oo to 15o μm of the water surface.

P. Valenta: Surface coverage is a property of the
                     adsorption equilibrium. As you are measuring
                     charging current differences it would be
                     more wise to indicate it directly on your
                     Fig. 1. to avoid misinterpretation.

Z. Kozarac: Surface coverage which we have used in Fig.1.
                     is the ratio between the adsorption effect
                     which is obtained for certain concentration
                     of surfactants at given experimental
                     conditions and maximum adsorption effect
                     which corresponds to completely covered
                     electrode surface. We do agree that adsorption
                     isotherms obtained by plotting surface cover-
                     age versus bulk concentrations in our cases

do not correspond to real thermodynamic isotherm, since the adsorption equilibrium is established only between the surface excess and the concentration of surfactants near the electrode surface which is considerably lower that the bulk concentration of surfactant.

H.W. Nürnberg: The inhibition effects produced by adsorbed surface active substances have to be well taken into account, as then no pretreatment of the sample, which would affect the speciation, is possible. However, in analytical determination of just the total dissolved amount of trace metals the above mentioned complications and interferences can be eliminated by appropriate pretreatment of the sample decomposing the organic matter, i.e., UV-irradiation.