THE EPR INVESTIGATION OF THE SORPTION PROCESS BY THE MARINE SEDIMENTS

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INTRODUCTION

The study of ions sorption process by marine sedi - ments has a great theoretical and practical importance because it offers the possibility to use these sediments in the de - polution processes.

The methods using radioactive isotopes [1,2] or chemical dosage [3] have the best results in the study of the sorption process.

The Electron Paramagnetic Resonance (EPR) represents a spectroscopic method of investigation,frequently used both in chemistry and solid state physics.This method,limited only to the study of the ions and radicals with paramagnetic properties,offers the possibility to determine rapidly the concentration of these paramagnetic species and to locate them in the host enviroment [4,5] .

Using the EPR tehnique in the study of the liquid samples,it becomes possible to determine rapidly the concentration of paramagnetic ions,due to the extremely short time measurement.This makes the EPR an efficient method in the study of the sorption processes.

This paper is devoted to the results obtained by studing the sorption process of Mn^{2+} ions,in aquous solution, by marine sediments.These results are compared with those, obtained in the same process by using the ^{56}Mn radioactive isotope [2,6].

EXPERIMENT

The investigated sediments were collected from the bottom of the Black Sea,at a depth of about 6 meters off Mangalia coast.The samples were fine grounded up to 60 μ and dried up at 105°C for 10 hours.

The mineralogical composition of the sediments,as determined by X ray diffraction,shows the predominance of calcite (more than 95 %).

The EPR measurements were performed at room temperature using a X band JEOL JES ME - 3X type spectrometer.The magnetic field sweep ratio was between 20 and 200 Gauss/minute.The EPR spectra were calibrated by means of a diphenil-picril-hydrazine (DPPH) standard sample.

The sorption process dynamics was investigated by measuring,at regular time intervals,the amplitude of the EPR lines of Mn^{2+} ions not sorped yet by the finely dispersed sediments in the solution.The time intervals were 15 minutes for the first 6 hours,60 minutes for the next 24 hours and finaly 24 hours for a period up to 175 hours.

The above mentioned experiment was performed using a $2 \cdot 10^{-2}$ mol/l solution of $MnCl_2$ in sea water.Both the sediments and the water samples were collected in the same place.The sediments concentration was 20 mg/cm^3 of solution.During the measurements,the solution containing finely dispersed sediments was continously stirred.Figure 1 shows the time variation of Mn^{2+} ions concentration remained in the solution.

The same measurements were performed by using a $2 \cdot 10^{-2}$ mol/l solution of $MnCl_2$ in distilated water.In the limit of experimentaly errors ,the results were similar (table 1).

RESULTS AND DISCUSSIONS

Analysing the curve shown in figure 1 one can see that the sorption process take place in two stages (part B and C of the curve).The numerical values of distribution k and diffusion D coefficients[+] as determined from the experimentaly curve are reproduced in table 1.

After about 3 hours (part A of the curve),until the completely dispersion of the sediment into solution,take place a very rapid decrease of Mn^{2+} ions concentration (part B of the curve).This process can be attributed to a dominant adsorbtion at the graines surface of sediments,up to their saturation.

For the diffusion coefficient D the value (in cm^2/s)

+) The k and D coefficients calculation was performed according to the method,presented in the paper [6].

$D_B = 1.21 \pm 0.15 \cdot 10^{-9}$ was established,what is in good agreement with an adsorbtion process.

About 30 hours after measurements started (part C of the curve),the Mn^{2+} ions concentration begin to decrease slowly.The diffusion coefficient D experimentaly determined for this process is $D_C = 1.27 \pm 0.1 \cdot 10^{-11}$.This process can be attribute to the slowly absorbtion of Mn^{2+} ions by sediments grains.

175 hours after introducing the sediments into solu - tion,the Mn^{2+} ions concentration decrease under 1 % from the initial value,wich is bellow the sesitivity limit of the EPR spectrometer.

In order to compare the efficiency of the EPR method, the global distribution and diffusion $\bar{k}$ and $\bar{D}$ coefficients were calculated,considering the total variation of Mn^{2+} ions concentration in solution.during the whole experiment (about 175 hours).Thus calculated values are very similar to those obtained using the radioactive isotope method [5,6] (table 1).

As a conclusion one can say that,by the EPR measure - ments,it was established the presence of of two different stages of the sorption process of Mn^{2+} ions by the sediments. These results pledge for the two layers model around a spherical grain,in a fihit source,proposed in ref. [7] .

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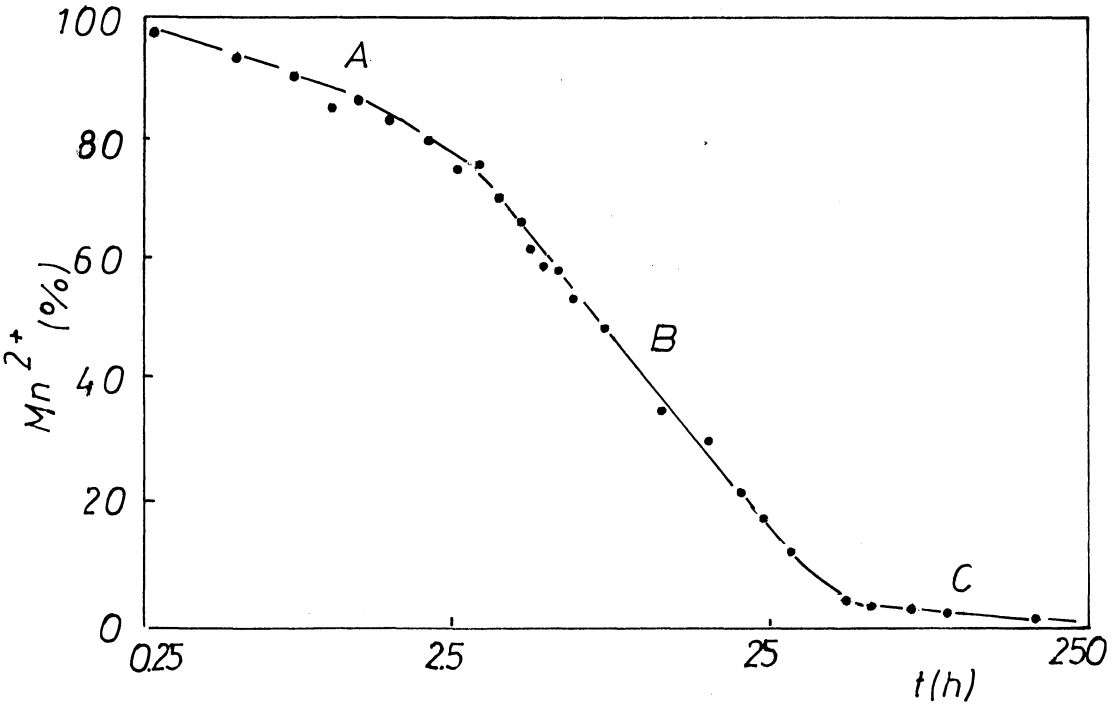
TABLE 1. The experimentaly determined values of the diss - tribution k and diffusion D (in cm^2/s) coefficients for the Mn^{2+} ions in sea (I) and distilated (II) water solutions. The values of the same coefficients reproduced from [5] for the ^{56}Mn iso - tope are also shown (III).

	I	II	III
k_B	$4.54 \pm 0.2 \cdot 10^3$	$5.6 \pm 0.3 \cdot 10^3$	
k_C	$4.33 \pm 0.2 \cdot 10^5$	$3.7 \pm 0.3 \cdot 10^5$	
$\bar{k}$	$3.0 \pm 0.2 \cdot 10^4$	$3.3 \pm 0.3 \cdot 10^4$	$5.75 \cdot 10^4$
D_B	$1.21 \pm 0.1 \cdot 10^{-9}$	$0.94 \pm 0.2 \cdot 10^{-9}$	
D_C	$1.27 \pm 0.1 \cdot 10^{-11}$	$1.48 \pm 0.2 \cdot 10^{-11}$	
$\bar{D}$	$2.0 \pm 0.1 \cdot 10^{-10}$	$1.8 \pm 0.2 \cdot 10^{-10}$	$2.75 \cdot 10^{10}$

CAPTION OF THE FIGURES

Figure 1. The time variation of the Mn^{2+} ions concentration in aqupus solution,in the presence of finely dispersed sediment.



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DULIU, O., VOLJIN, V.

"The EPR investigation of the sorption process by the marine sediments"

Paper presented by R. Mihnea (Romania)

Discussion

No comment.