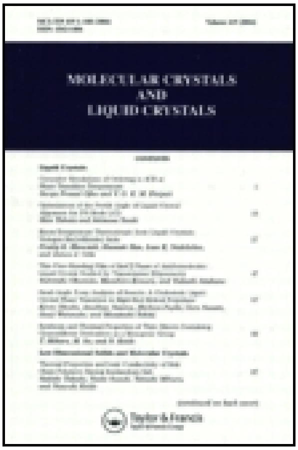

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CALORIMETRIC AND POTENTIOMETRY INVESTIGATIONS OF THE ACCEPTOR COMPOUNDS INTERCALATIONS INTO GRAPHITE

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Abstract In the work the intercalation of H_2SO_4 (from 98% to 76%) into graphite (oxidizer -$(NH_4)_2S_2O_8$) was investigated by potentiometry. It was established that the redox potential of oxidizer solution depends on the concentration of H_2SO_4. The criterion for the formation of graphite hydrogenosulfate[1] (GHS) was corroborated by the experiment. It was shown that stage of GHS is determined by the redox potential of the oxidizer solution. The system C-$K_2Cr_2O_7$-94% H_2SO_4 was investigated by calorimeter and potentiometer methods in situ. The "overoxidation" of stage 1 GHS was observed during the calorimetric investigation (the second exo-effect) but not seen on the potentiometry curve. It was proposed that more high oxidation of graphite and the formation of ion-covalent bonds take place during "overoxidation".

INTRODUCTION

In our work[1] we assumed that the stages of GHS depend on redox potential of oxidizer solution in H_2SO_4. It was proposed to use the standard redox potential scale to choose the oxidizers for the formation of a given stage GHS. It was established that the strong oxidizer $(NH_4)_2S_2O_8$ (E_o= 2,01 V) is not resistant to 96% H_2SO_4 and only stage 2 was obtained in this solution.We expected that the redox potential of the solutions of $(NH_4)_2S_2O_8$ in H_2SO_4 of different concentrations would change in a wide range. For the experimental verification of the criterion for the formation of GHS (the dependence of stages GHS on redox potential of oxidizer solution[1]) we studied the intercalation of H_2SO_4 into graphite by potentiometry, using the solutions of $(NH_4)_2S_2O_8$ in H_2SO_4 (the concentration of acid changed from 98 to 76%). Unfortunately, $(NH_4)_2S_2O_8$ instability in aqueous acid solutions does not allow to determine the intercalation reaction enthalpy by calorimeter.

In the work[2] we showed, that there are two exo-effects on the time dependence of the heat flow (system C-$K_2Cr_2O_7$-94% H_2SO_4): the first corresponds to the formation of GHS of different stages and the second - to the "overoxidation" of stage 1 GHS. It was interesting to study these processes by calorimeter and potentiometer methods in situ.

EXPERIMENTAL

The calorimetric and potentiometry methods are described in the work[3]. Graphite plates (HOPG) with mass 7-8 mg were used for the synthesis. The redox potentials of oxidizer solutions were measured in H-shaped glass cell. The platinum wire is used as the indicator electrode. The reference electrode was Hg/Hg_2SO_4 filled with x% H_2SO_4 and connected to the oxidizer solution by a Luggin capillary. The potential measuring was carried out with a constant-current digital voltmeter.At solution preparation 0,7 g of $(NH_4)_2S_2O_8$ was added to 10 cm^3 of x% H_2SO_4.The redox potential of the solution with time was continuously recorded.During the investigations by the calorimetric and potentionmetry methods in situ (system C-$K_2Cr_2O_7$ - 94% H_2SO_4) the cell with Hg/Hg_2SO_4, 94% H_2SO and graphite on the Pt wire in the solution of $K_2Cr_2O_7$ in 94% H_2SO_4 is placed into the calorimeter. We dissolved 1,7 g of $K_2Cr_2O_7$ in 100 cm^3 94% H_2SO_4. The rations used: $K_2Cr_2O_7/C = 0,223$; $(NH_4)_2S_2O_8/C = 3,4 \div 4,4$. The reaction products were investigated by x-ray diffraction (Cu K_α radiation).

RESULTS AND DISCUSSION.

Fig. 1 shows the time dependencies of the currentless redox potentials of the solutions of ($NH_4)_2S_2O_8$ in x% H_2SO_4 ($E_{Hg_2SO_4}$). One can see from Fig.1 that the redox potentials of$(NH_4)_2S_2O_8$ are decreasing with dilution of H_2SO_4. On Fig.1 the potential ranges ($E_{Hg_2SO_4}$) for the formation of different stages of GHS are shown as well. The examination of these results show that the formation of stage 1 would take place in 98% H_2SO_4, stage 2 - in 94%, stage 3 - in 89% H_2SO_4 and higher stages in 86% H_2SO_4

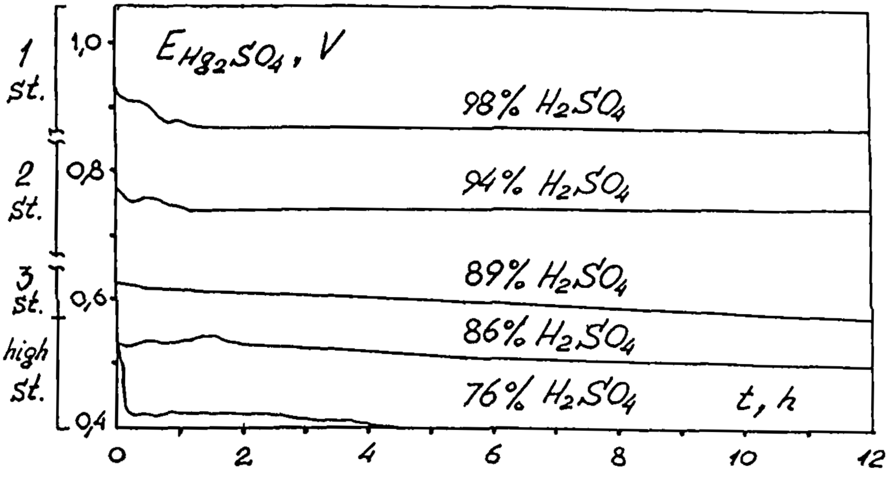

FIGURE 1.Time dependencies of the redox potentials of the solutions of $(NH_4)_2S_2O_8$ in x% H_2SO_4.

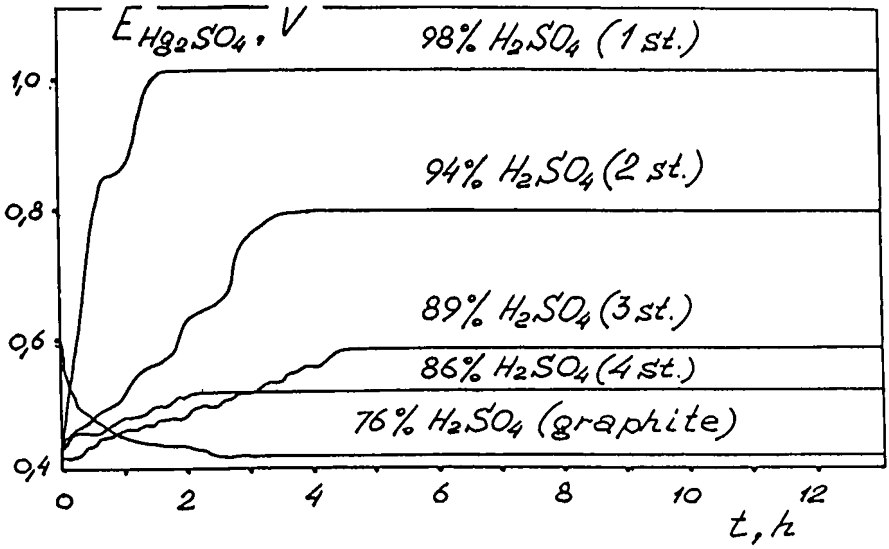

FIGURE 2. Time dependencies of the potentials of graphite in the solutions of H_2SO_4 of different concentrations (oxidizer - $(NH_4)_2S_2O_8$).

and 76% H_2SO_4. These our estimations agree with the experimental results on the Fig.2. As expected we obtained stage 1 (98% H_2SO_4), stage 2 (94% H_2SO_4), stage 3 (89% H_2SO_4), stage 4 (86% H_2SO_4) and there was no intercalation in 76% H_2SO_4. So,these results corroborated the conclusion about the dependence of GHS stages on the redox potentials of oxidizer solutions[1], and agree with the work[4].

In Fig.3 the time dependencies of heat flow and potential of graphite (in situ) are shown for system C-$K_2Cr_2O_7$ - 94% H_2SO_4. As can be seen the "overoxidation" of the 1 stage of GHS is observed on the curve of heat flow (the second exo-effect), but not seen on the potentiometry curve.

This can be explained by the formation of the ion-covalent bonds between graphite macrocation and intercalate. This conclusion is confirmed by the results of the investigation of the reaction in C - $K_2Cr_2O_7$-94% H_2SO_4 system by electric conductance method.

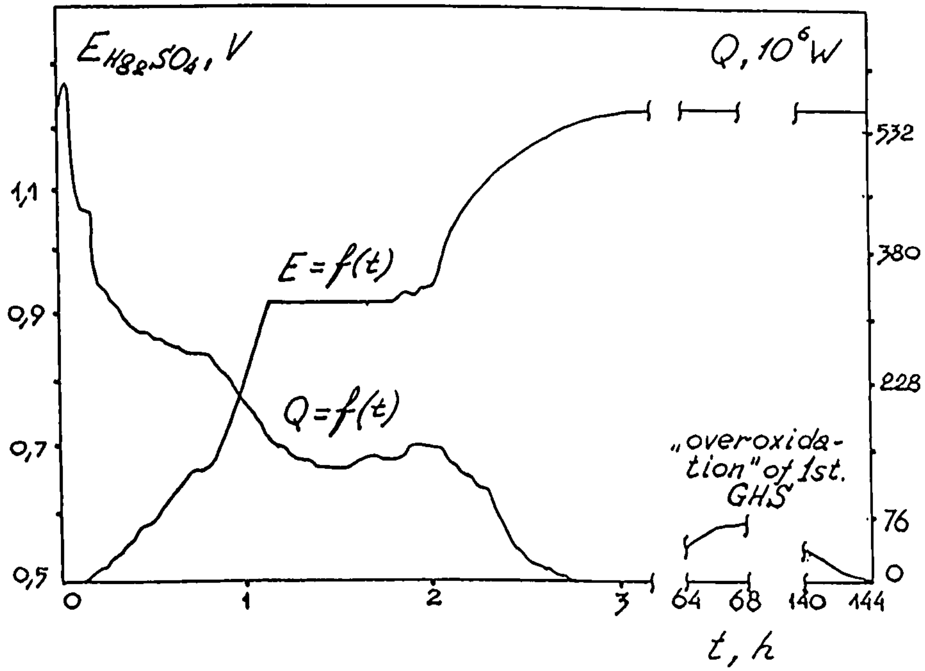

FIGURE 3 Time dependencies of the heat flow and potential of graphite (in situ) with $K_2Cr_2O_7$ oxidation in 94% H_2SO_4.

The work deals with the investigation of the variations of the electric conductance in the basal plane of HOPG (σ_a) during the intercalation of H_2SO_4 (oxidizer - $K_2Cr_2O_7$). The resistance was measured by four contact method with direct current. The Pt wire used as a press down contact. It is shown, that after the formation of the first stage of GHS, the monotone increase of resistance is observed up to the values several times higher than for initial graphite sample. This effect is caused by the decrease of the free current carriers relaxation time, that is the increase of defects number in carbon layers as a result of covalent bonding of carbon atoms with intercalated molecules. This fact is confirmed by x-ray in situ data. The first stage GHS in excess $K_2Cr_2O_7$ results at first in partial and further in complete amorphization.

REFERENCES

1. V.V.Avdeev, L.A.Monyakina, I.V.Nikol'skaya, N.A.Sorokina and K.N.Semenenko, Carbon, 30, 819, 1992.

2. L.A.Monyakina, I.V.Nikol'skaya, N.E.Sorokina and V.V.Avdeev, Ext. Abstr. Program-Bienn. Conf. Carbon, 1991, 20th, 686.

3. V.V.Avdeev, L.A.Monyakina, I.V.Nikol'skaya, N.E.Sorokina, K.N.Semenenko,and A.I.Finaenov, Carbon, 30, 825,1992.

4. M.Inagaki, N.Iwashita and E.Kouno, Carbon, 28, 49, 1990.