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THE HEAT OF IMMERSION OF NATURAL MAGNETITE IN AQUEOUS SOLUTIONS*

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ABSTRACT

The heat of immersion of natural magnetite in aqueous solutions has been determined by the isothermal differential microcalorimeter ($\Delta H_i = -646 \pm 25$ erg cm^{-2}). The zero point of charge of natural magnetite was also determined ($pH_{zpc} = 6.5$). The value obtained for the heat of immersion is a linear function of the zero point of charge of the natural magnetite examined.

INTRODUCTION

Magnetite, as a material for the purification of cooling water from BWR and PWR reactors, was investigated by researchers from Oak Ridge National Laboratory[1–4]. Adsorption properties of magnetite were investigated in various solutes by Anderson[5], Benton and Horsfall[6], Iguchi and Inouye[7], Shimoizaka[8], Fujigaki et al.[9], and Schneider[10]. Recently, a series of papers dealing with the determination of adsorption on natural magnetite from aqueous solutions for various nuclides[11–13] were published by authors from our laboratory.

In order to continue the study of adsorption processes on natural magnetite, experiments involving the determination of the heat of immersion, as well as of the zero point of charge of natural magnetite, were carried out.

EXPERIMENTAL

Experiments were performed on natural magnetite supplied by the mine "Rudna Glava" in Eastern Serbia. The magnetite ore was ground and sieved on a 100–150 mesh sieve. The fraction was treated with 2M HNO_3 followed by water washing until neutral reaction (pH ~ 6.5) and dried at 110°C.

The content of natural magnetite applied in our work was determined by chemical analysis and was as follows: $Fe_2O_3 \cdot FeO = 93.56\%$; $SiO_2 = 2.40\%$; $Al_2O_3 = 0.91\%$; $MgO = 0.12\%$ and $NiO = 0.11\%$.

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*This work represents a part of the M. Sc. Thesis of the author S.K.M., to whom correspondence should be addressed.

The surface area of the magnetite fraction was determined by the Ströhlein areameter using dry nitrogen (purity 99.9%). The value of 0.9 m^2 g^{-1} was obtained.

The isothermal differential microcalorimeter was used for the determination of the heat of immersion of magnetite in aqueous solutions[14,15].

The method described by Herczynska[16] and Laskowski and Sobieraj[17] was applied for the determination of the zero point of charge. In our experiments, samples of magnetite were shaken for 24 h with 50 ml of 0.1 N KCl solution, in PVC vessels. Initial pH values were obtained by adding an amount of HCl or KOH solutions, keeping the ionic strength constant. The amount of H^+ (or OH^-) ions adsorbed by magnetite was calculated from the difference between the initial and final concentrations of H^+ (or OH^-) ions. For the determination of the concentration of H^+ (or OH^-) ions, a Beckman pH-meter (Research Type) was used.

RESULTS AND DISCUSSION

The results obtained for the measurement of the zero point of charge are given in Figs. 1 and 2. It is obvious that for natural magnetite in aqueous solution this point is at pH = 6.5. Determination was performed in NaCl and KCl solutions. It can be seen that the same value is obtained in both runs. This leads to the conclusion that no difference exists between K^+ and Na^+ ions as cations of an indifferent electrolyte. This ought to be expected since neither Na^+ nor K^+ ions are adsorbed on magnetite from aqueous solutions. Therefore, the potential of the magnetite surface can be determined only by H^+ and OH^- ions. This is well known from the literature[18].

Figure 3 shows the change of the initial pH values after equilibration (for 24 h) of magnetite in solutions. It is evident that, for the initial pH values in the range

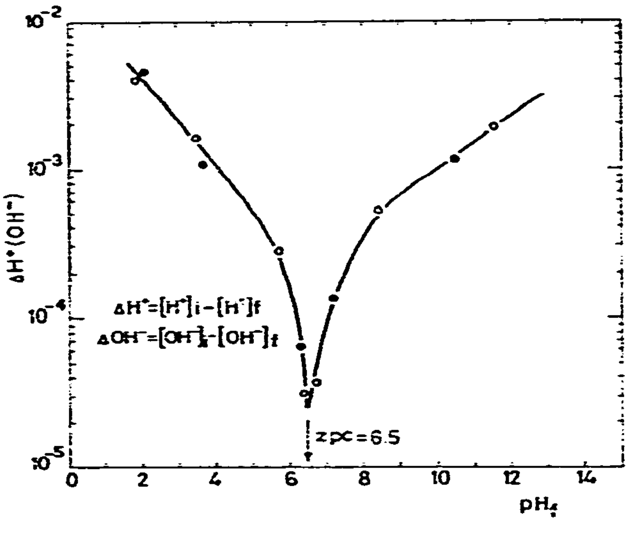

Fig. 1. Adsorption of H^+ (left curve) and OH^- (right curve) on natural magnetite from the solutions of NaCl (○) and KCl (●) as a function of the final pH of the solution.

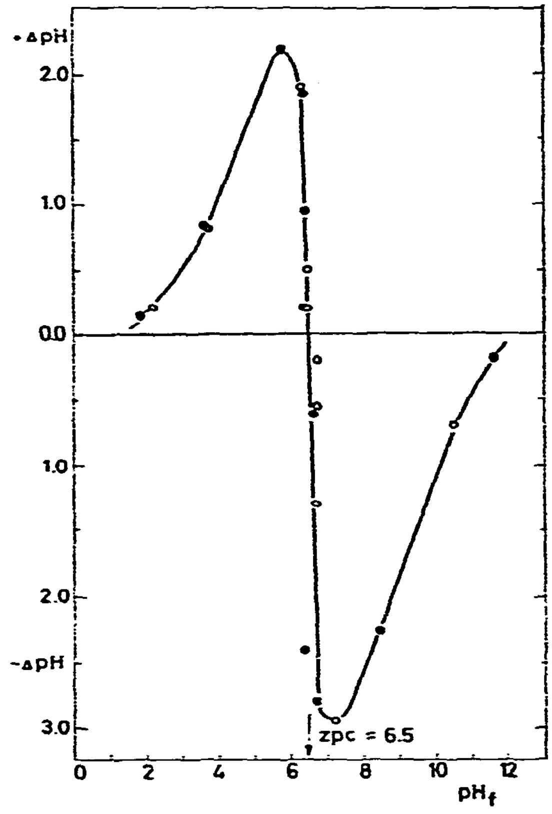

Fig. 2. Determination of the zero point of charge by plotting $\Delta pH = pH_f - pH_i$ versus pH_f ($t = 23 \pm 1$ °C). 0.1 N NaCl (○); 0.1 N KCl (●).

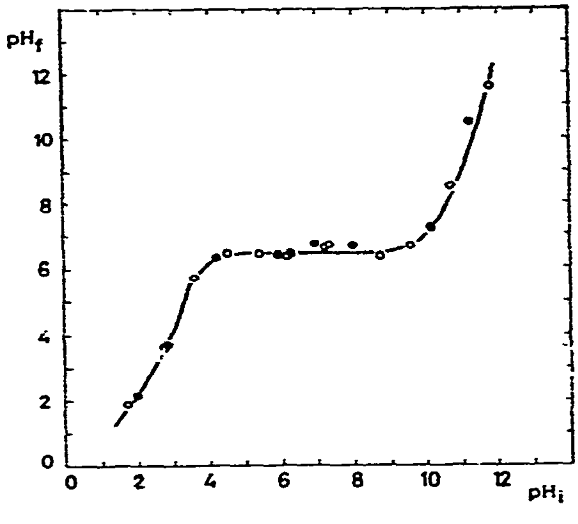

Fig. 3. The change of pH of 0.1 N NaCl (○) and 0.1 N KCl (●) solutions after equilibration with natural magnetite. (pH_f – final value; pH_i – initial value.)

$4 < pH < 9.5$ the final pH is about 6.5, which is very close to the value obtained for the zero point of charge of the magnetite.

The values of the zero point of charge of the magnetite obtained by various authors are presented in Table 1.

TABLE 1

THE VALUES FOR THE ZERO POINT OF CHARGE OF MAGNETITE

$(pH)_{zpc}$	*Method used*	*Literature*
6.5	Electrophoresis	19
6.5	Adsorption of H^+ and OH^- ions	17
7.1[a]	Adsorption of H^+ and OH^- ions	9
6.5	Adsorption of H^+ and OH^- ions	this work

[a] In this case the value is somewhat higher due to the author presenting the results of adsorption of H^+ and OH^- ions as a function of the initial pH value.

The isothermal differential microcalorimeter was calibrated by the determination of the heat of solution of KCl in water, the integral heat of which, obtained at infinite dilution in our runs, $\Delta H = 4190 \pm 44$ cal mol^{-1}, is in good agreement with the literature values[20].

The heat of immersion of magnetite in water $\Delta H_i = -0.140 \pm 0.005$ cal g^{-1}, i.e. $\Delta H_i = -646 \pm 25$ erg cm^{-2} at 25°C was calculated from calorimetric measurements. Its dependence on the amount of magnetite used is shown in Fig. 4. The heats measured were corrected for the thermal effect produced by ampule breakage, which was $\Delta h_b = -0.10 \pm 0.03$ cal. Our value is in good agreement with that obtained by Okado et al.[21] ($\Delta H_i = -519 \pm 3$ erg cm^{-2} at 25°C). Slight difference between these two values can be attributed to the difference in the magnetites used.

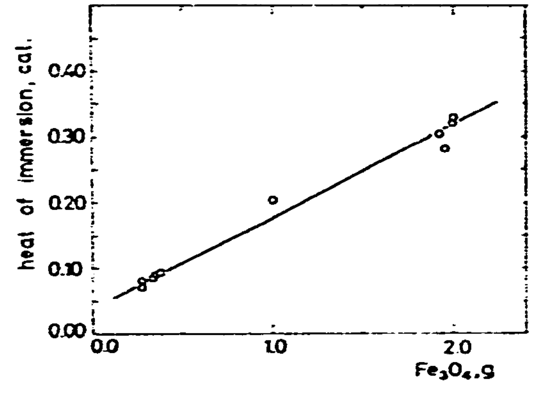

Fig. 4. The dependence of the heat of immersion on the amount of natural magnetite.

It was shown in the literature[22] that the heats of immersion of various oxides are in the range 100–1000 erg cm^{-2}, while the zero points of charge for the same oxides are in the range from pH = 1 to pH = 10.

The dependence of the heat of immersion on the zero point of charge is given by the following equation[22]:

$$(-\Delta H_i) = 4.606\,RT(\mathrm{pH})_{zpc} + (-\Delta H_c) \qquad (1)$$

R and T have the usual meaning, while $(-\Delta H_c)$ is constant for the set of oxides–water and equivalent to the heats of immersion of an oxide with the zero point of charge of pH = 0, i.e. $a_{H_0^+} = 1$.

The interrelation of the heats of immersion $(-\Delta H_i)$ in water and zero points of charge (pH_{zpc}) of oxides is presented in Fig. 5, from which it is evident that a straight line is obtained. Our values, obtained in the runs with natural magnetite, fit quite well in the set of data presented in Fig. 5.

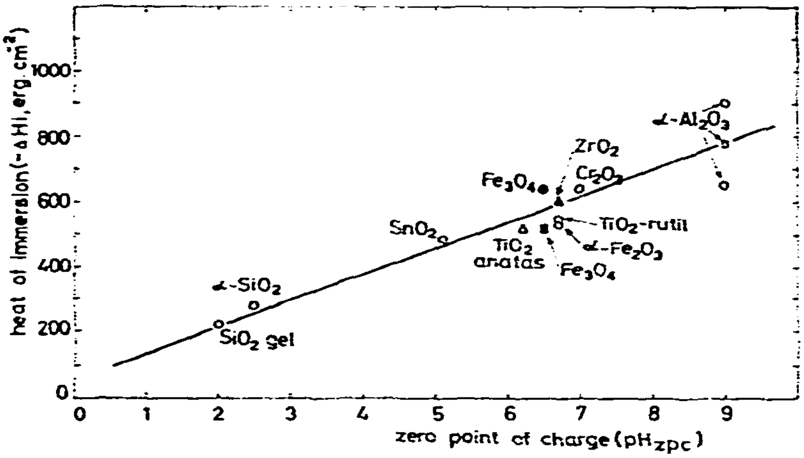

Fig. 5. The interrelation of the heats of immersion $(-\Delta H_i)$ in water and the zero points of charge (pH_{zpc}) of the oxides. ○, ref. 22; ■, ref. 21; Δ, refs. 23 and 24; ▲, refs. 23 and 24; □, ref. 25; ●, our work.

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