Thermochimica Acta, 92 (1985) 317-320
Elsevier Science Publishers B.V., Amsterdam

CALORIMETRIC STUDIES FOR THE ENTHALPY OF DISPLACEMENT BY ADSORPTION FROM AQUEOUS SOLUTION

Reinhard Zimmermann*, Herbert A. Schneider
Bergakademie Freiberg, Sektion Physik
Gert Wolf
Bergakademie Freiberg, Sektion Chemie
9200 Freiberg, GDR

ABSTRACT

Calorimetric measurements of enthalpy of displacement in solution of pyridine on Al_2O_3 as well as 2-phenylethylenephosphonic acid (SPS) on SnO_2 were performed by variation of pH and concentration of solution. The determination of the adsorbed amount permits the calculation of molare enthalpies.

INTRODUCTION

The calorimetric technique is an excellent method to measure temperature changes during the process of adsorption in the solid-liquid interface and to determine enthalpies of the adsorption process in a direct way. Enthalpies of displacement reflect energetical interactions between the solid and the adsorbed molecules as well as between the molecules of the interface and those of solution, too.

Adsorption phenomena at solid-water interface are controlled in most cases by the electrical double layer /1/. Hydrogen and hydroxyl ions are of special importance for the electrical proporties of the interface in the case of oxides /2/.

The electrical proporties of the interface are also influenced during the process of adsorption. Therefore characteristic adsorption enthalpy isotherms result.

In connection with measurements of the adsorbed amount it is possible to calculate molare enthalpies and to discuss them in regard of the structure of the interface.

MEASURING METHODS

γ-Al_2O_3 ($A = 103\ m^2 \cdot g^{-1}$, Point-of-Zero-Charge PZC = 7,7) and two types of synthetic SnO_2 (1. $A = 160\ m^2 \cdot g^{-1}$, PZC = 4,1; 2. $A = 184\ m^2 \cdot g^{-1}$, PZC = 4,2) were used as adsorbents.

Proceedings of ICTA 85, Bratislava

The specific surface areas were determined by a BET-method. Both charges of SnO_2 are products of precipitation of stannic chloride with ammonia. Pyridine, purity p. A., and 2-phenylethylene-phosphonic acid (SPS), purity > 99 %, were used in form of aqueous solutions.

The pH of sulutions was adjusted by addition of NaOH or HCl.

The enthalpies of displacement were determined with the commercial precision calorimetry system LKB 8700 and a new calorimetric vessel using also the technique of breaking special glass ampoules /3/. The glass ampoule was filled with 0,5 g Al_2O_3 or 1 g SnO_2 and always 1 ml water to suppress a wetting reaction.

The heat of breaking off a ampoule was determined to $\Delta h = -57 \pm 8$ mJ /3/.

The calorimetric vessel was always filled with 80 ml solution.

The adsorption isotherms were measured under comparabel conditions in the same way as calorimetric measurements by determining the concentration of solution before and after the adsorption experiment by an UV-spectral-photometric method.

RESULTS AND DISCUSSION

The adsorption from solution on the oxides is influenced significantly by the value of pH of the solution. If pH is greater than PZC of Al_2O_3 or of SnO_2, then the adsorption of both used adsorptives is hindered. The decrease of pH of solution below PZC yields an enhancement of the amount of adsorbed molecules and the enthalpy of displacement, because more and more hydroxyl ions are desorbed into solution and dissociated adsorptives $R\text{-}PO(OH)O^-$-ions or pyridine-molecules are able to occupy the positive charged places in the interface of the oxids.

The results are also used to optimate the pH of solution for the measurements versus molare fraction of adsorptive X_2. The measurements of the system Al_2O_3-Pyridine were performed with pH = 4,0 and these of SnO_2-SPS with pH = 2,5. The measuring accuracy of the pH of solution (Δ pH = ± 0,05) yields an error of $\Delta_a H$ of about five per cent.

The results of calculation of molare enthalpies of displacement $\Delta_a H_m$ are shown in Figure 1. The molare enthalpies of displacement of both adsorption systems are decreased in a similar way by increasing amount of adsorptives on the surface.

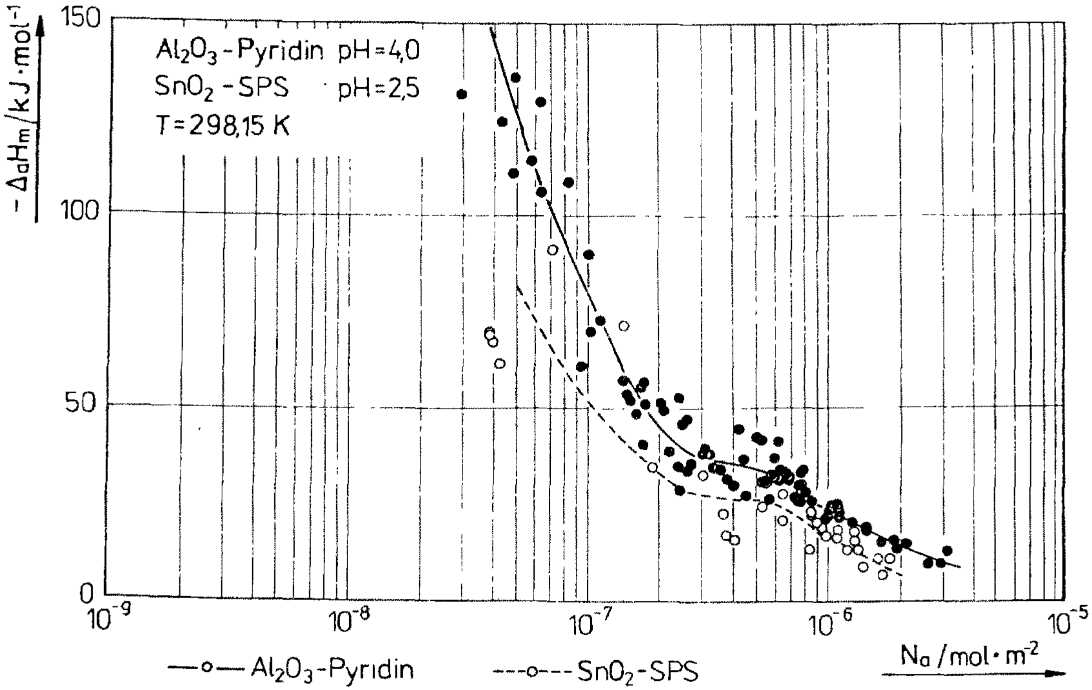

Fig.1: Molare enthalpy of displacement versus amount of adsorbed molecules

Differences in the absolute values of $\Delta_a H_m$ are based on different pH of solutions. Three characteristic ranges can be seen in the plot of $\Delta_a H_m$ versus N_a. The first one with high values of $\Delta_a H_m \geq -35$ kJ · mol^{-1} can be interpreted with chemical bonds between the nitrogen of pyridine and the positive alumina-ions of Al_2O_3 respectively between ions of SPS and stannic-ions Sn^{4+} of SnO_2.

The second range with $\Delta_a H_m$ between -25 to -35 kJ · mol^{-1} shows a small slope. There exist no strong energetical interaction with the surface like chemical bonds in the first range. The third range is characterized by very low values of $\Delta_a H_m$ (< -20 kJ · mol^{-1}). It is possiblethat hydroxyl ions on the surface are not displaced by the adsorptives. The adsorptives are adsorbed on the layer of hydroxyl ions or as a second layer of adsorptives. Physical interactions are of importance in this range.

CONCLUSIONS

The results of the calorimetric measurements characterize the surfaces of Al_2O_3 and SnO_2 used as very heterogeneous ones in regard of energetical interactions with the different compounds of the aqueous solution. The descriped calorimetric technique is suitable for investigations of adsorption in solutions which are very important for technical processes such as flotation of ores or minerals.

REFERENCES

/1/ FUERSTENAU, D. W.; RAGHAVAN, S.:
Reprinted from: Flotation, A.M. Gaudin Memorial
Volume, M.C. Fuerstenau, Ed.
AIME, New York, 1976

/2/ FUERSTENAU, D. W.; HEALY, T.W.
in "Adsorptive Bubble Separation Technique", R. Lemlich
Ed., Acad.Press Inc., New York, Chapter 6, pp. 92-131(1972)

/3/ ZIMMERMANN, R.; WOLF, G.; SCHNEIDER, H.A.
Colloids & Surfaces: in press