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HEATS OF IMMERSION OF TITANIUM DIOXIDE PIGMENTS IN AQUEOUS SOLUTIONS

PART II. THE IMMERSION OF DRIED RUTILE PIGMENT IN SOLUTIONS OF VARYING SOLUTE CONCENTRATION

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ABSTRACT

The heats of immersion of a partially-dried coated rutile pigment in water and aqueous solutions of several surfactants were measured by a differential calorimetric method. The variations in heats of immersion with solute concentration are interpreted in terms of a theoretical model involving the heats of adsorption of water and solute. The heats of immersion were more exothermic in the solutions than in water itself although it is not certain whether the solute is adsorbed on top of a fully adsorbed water complement or whether competitive adsorption between water and the solute occurs.

INTRODUCTION

Whenever the surface of a solid comes into contact with a non-reactive liquid or solution a thermal effect is observed which is termed the *heat of immersion* or *the heat of wetting*. The measurement of the heats of immersion provides a useful method of investigating the interaction of the solid surface with the liquid or solution into which the solid is immersed[1]. In a previous paper[2] the heats of immersion in water and aqueous surfactant solutions of partially dried and air-conditioned titanium dioxide pigments were reported. The results were successfully treated by a Hess's law approach and the heat of adsorption of physically adsorbed water on the pigments was calculated. The work generally indicated an absence of capillary condensation of *physically* adsorbed water on the anatase and rutile pigments investigated.

While the heats of immersion of titanium dioxide have been measured for a variety of systems[3–8], in all cases the samples of solid were thoroughly dried at temperatures up to 500°C and also outgassed at low pressures. Such treatments of commercial titanium dioxide pigments would significantly impair their usefulness and the results are not relevant in the industrial situation. The purpose of the present work was to investigate the heats of immersion of commercial rutile pigment which possessed a coating of alumina, silica and zinc oxide. The coating on the rutile improves its dispersibility in paints and also minimises the effects of photo-initiated degradation of the resultant paint film. For this work the pigment samples, which had been in equilibrium with water vapour under ambient laboratory conditions (nominally 25°C), were superficially dried at 140°C for several hours at atmospheric pressure.

In the work previously reported[2] the heats of immersion were measured in solutions whose surfactant concentrations were mainly 0.1 molar. In this work the measurements were carried out with concentrations of solute ranging from 10^{-4} molar to 1 molar. The solutes used were potassium propionate, potassium octoate, potassium stearate, potassium oleate, propionic acid, sodium benzene sulphonate, sodium lauryl sulphonate, cetyl trimethyl ammonium bromide, and ethyl alcohol.

EXPERIMENTAL

The calorimeter used in this work was of the differential type and its construction and method of operation have been described previously[2]. The rutile pigment was that used previously[2] and possessed a surface area of 11.1 $m^2 g^{-1}$ and was fairly porous. The composition of the coated rutile prior to drying was ZnO 1.02%, Al_2O_3 2.15%, SiO_2 1.12%, the remainder being titanium dioxide and adsorbed water. The water content of the pigment was measured by thermogravimetric analysis and also by the Karl–Fischer method, and the results are summarised in Table 1. The thermogravimetric results showed that the rutile possessed a considerable amount of adsorbed water which was quite difficult to remove (in contrast to the anatase used previously[2]). The retentive power of the rutile for water may well be due to the porous nature of the pigment coating. This view was supported by the Karl–Fischer measurements.

TABLE 1

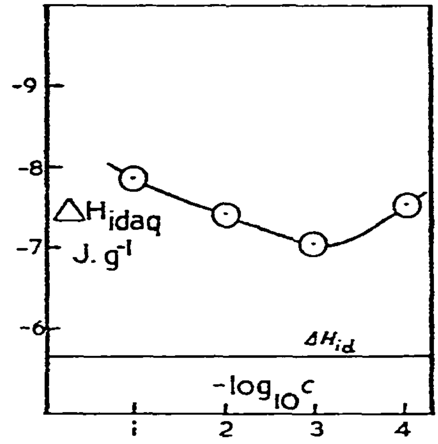
DETERMINATION OF THE WATER CONTENT OF THE COATED RUTILE PIGMENT

Method	*Water content (mg H_2O per gram of pigment)*
(a) *TA method*	
(i) 4 hours at 140°C	13.2
(ii) 1½ hours at 550°C	19.4
(b) *Karl–Fischer method*	
(i) dioxan solvent	8.2
(ii) methanol solvent	11.8

For all the measurements reported here the pigment was dried at 140°C for several hours prior to use and is referred to as dried pigment (S_d) in spite of the fact that the rutile still possessed adsorbed water after this treatment. If the approximate area of a water molecule is taken as 10^{-19} m^2 then the air-conditioned rutile would possess the equivalent of approximately six molecular layers of water. After drying at 140°C for several hours the dried rutile still possessed approximately two molecular layers of adsorbed water.

RESULTS AND DISCUSSION

The heat of immersion of the dried rutile (S_d) in water, *i.e.*, ΔH_{id}, was -5.7 J g^{-1}. The heats of immersion of the dried rutile in various aqueous solutions (ΔH_{idaq}) are plotted as a function of the logarithm of the solute concentration in Figs. 1–9.



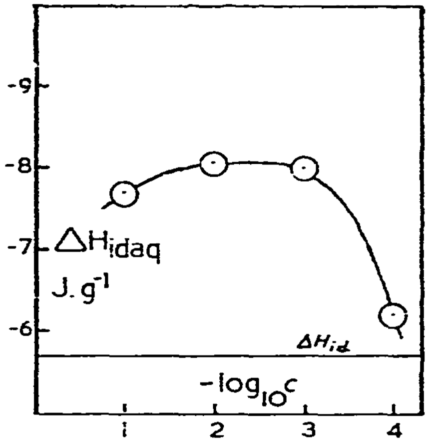
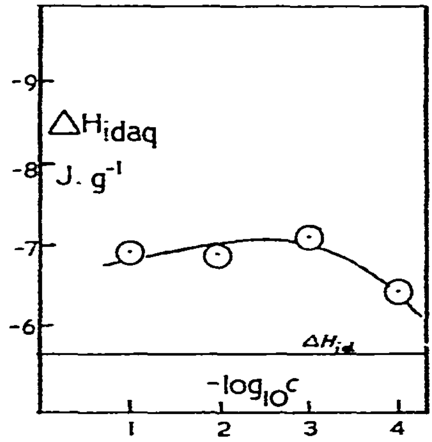


Fig. 1 (left). Heat of immersion of rutile in potassium propionate solution.

Fig. 2 (right). Heat of immersion of rutile in potassium octoate solution.



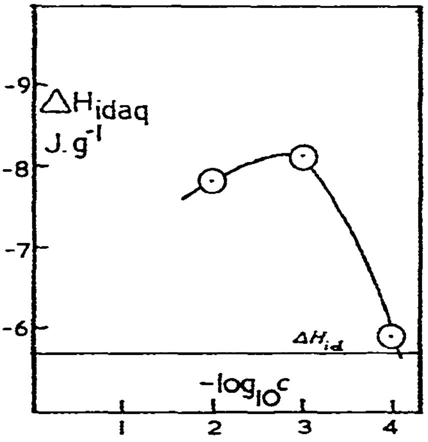
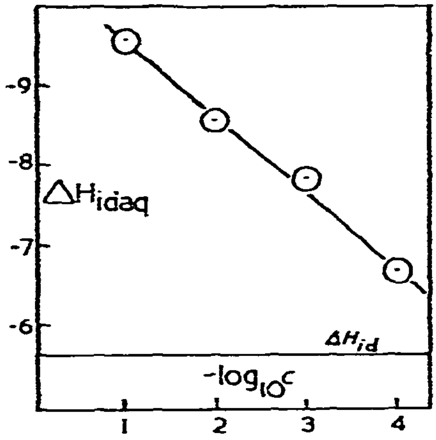


Fig. 3 (left). Heat of immersion of rutile in sodium benzene sulphonate solution.

Fig. 4 (right). Heat of immersion of rutile in potassium stearate solution.



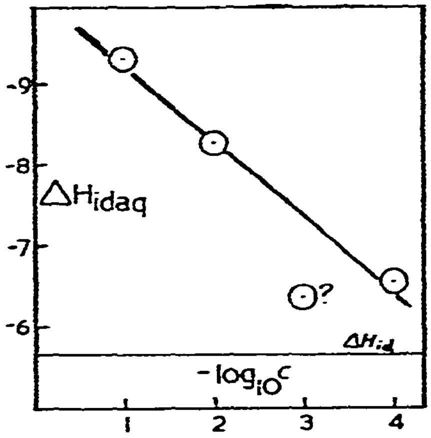
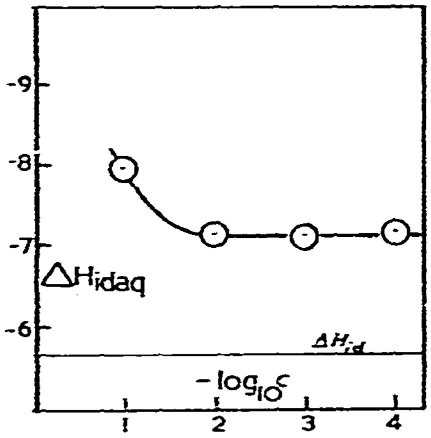


Fig. 5 (left). Heat of immersion of rutile in propionic acid solution.

Fig. 6 (right) Heat of immersion of rutile in potassium oleate solution.



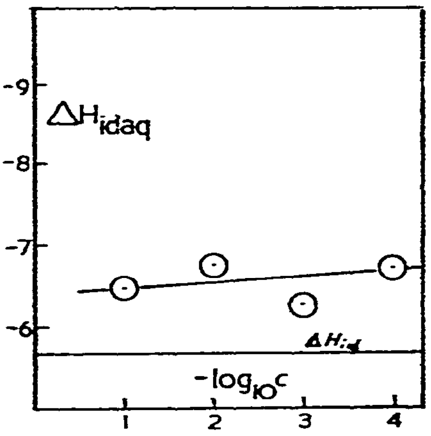


Fig. 7 (left). Heat of immersion of rutile in cetyl trimethylammonium bromide solution.

Fig. 8 (right). Heat of immersion of rutile in sodium lauryl sulphonate solution.

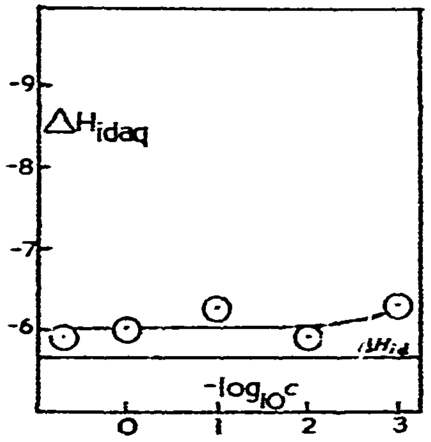


Fig. 9. Heat of immersion of rutile in ethyl alcohol solution.

When a solid is immersed in a solution containing n_A mol of a solute A not only will solvent be adsorbed but adsorption of solute may also occur. If the solute is adsorbed on some sites that would have been occupied by water molecules had the immersion been in pure water, then the heat change due to the *interaction of water* in the solution with the solid will be less than ΔH_{id} by an amount of heat equivalent to the water displaced from the surface by the adsorbed solute. The heat of interaction of water *from the solution* with the solid may be represented as $\Delta H'_{id}$. The heat change due to the adsorption of the solute will be a function of the amount of solute adsorbed. Thus the heat of immersion of a dried pigment in an aqueous solution will be given by[2]

$$\Delta H_{idaq} = n'_A \Delta H_a + \Delta H'_{id} \tag{1}$$

where ΔH_a is the molar heat of adsorption per gram of pigment and n'_A is the number of moles of solute adsorbed per gram of pigment.

If, when dry pigment is immersed in water, there are n_1 mol of water per gram of pigment involved in the interaction to produce the heat change ΔH_{id}, then

$$\Delta H_{id} = n_1 \Delta H_w$$

where ΔH_w represents the molar heat of adsorption of water per gram of pigment. If, on the other hand, when the dry pigment is immersed in a solution there are n_2 mol of water involved in the corresponding interaction, then

$$\Delta H'_{id} = \frac{n_2}{n_1} \Delta H_{id}. \tag{2}$$

Substitution for $\Delta H'_{id}$ in eqn (1) leads to

$$\Delta H_{idaq} = n'_A \Delta H_a + \frac{n_2}{n_1} \Delta H_{id}. \tag{3}$$

If each molecule of solute adsorbed on the pigment takes the place of one water molecule, (*i.e.* water is competing on a *one to one* basis), then $n_2 = n_1 - n'_A$. Substitution for n_2 in eqn (3) leads to the expression

$$\Delta H_{idaq} = n'_A \left(\Delta H_a - \frac{\Delta H_{id}}{n_1} \right) + \Delta H_{id} \tag{4}$$

or

$$\Delta H_{idaq} = n'_A (\Delta H_a - \Delta H_w) + \Delta H_{id}. \tag{5}$$

If however, each molecule of solute adsorbed occupies the space of Q water molecules on the surface of the solid then eqn (4) would become

$$\Delta H_{idaq} = n'_A \left(\Delta H_a - \frac{Q}{n_1} \Delta H_{id} \right) + \Delta H_{id}. \tag{6}$$

In the above equations we have assumed that the adsorbed solute is adsorbed competitively with water. Another possibility exists, namely, adsorption of solute *on top of a full complement of adsorbed water*. In this case $n_2 = n_1$ and therefore $\Delta H'_{id} = \Delta H_{id}$, which means that eqn (1) would become

$$\Delta H_{idaq} = n'_A \Delta H_a + \Delta H_{id}. \tag{7}$$

Eqns (4), (6) and (7) thus represent three possible situations; (a) competition of one molecule of solute with one molecule of water for adsorption sites, (b) competition of one molecule of solute with Q molecules of water for adsorption sites, and (c) adsorption of solute on top of a full complement of adsorbed water.

In the latter case eqn (7) is the appropriate equation. If adsorption of solute *on top* of adsorbed water is fairly simple then one would expect the variation of ΔH_{idaq} with concentration of solute (c) to be of the form shown in Fig. 10. As c increases so will n'_A increase and hence cause an increase in ΔH_{idaq}.

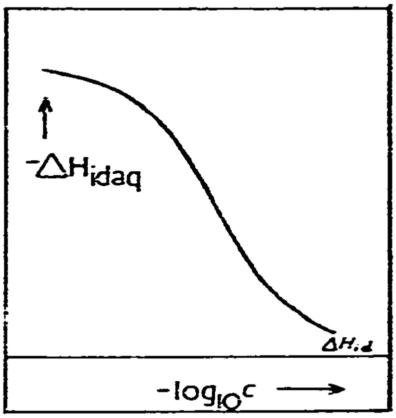
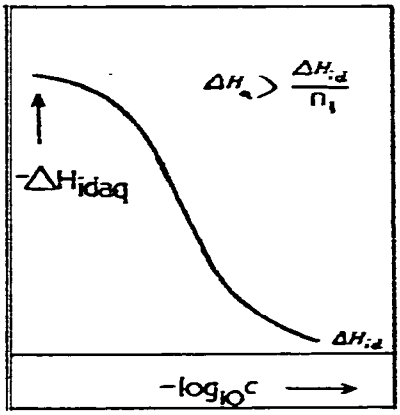


Fig. 10. Schematic representation of eqn (7).



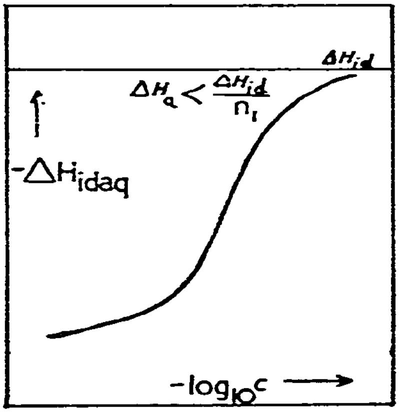


Fig. 11 (left). Schematic representation of eqns (4) and (6) with $\Delta H_a > \Delta H_{id}/n_1$ or $\Delta H_a > Q\Delta H_{id}/n_1$.

Fig. 12. (right). Schematic representation of eqns (4) and (6) with $\Delta H_a < H_{id}/n_1$ or $\Delta H_a < Q\Delta H_{id}/n_1$.

If, however, the adsorbed solute enters into competition with water then $\Delta H'_{id} \neq \Delta H_{id}$ and the appropriate equations are (4) and (6). In the case of $\Delta H_a > \Delta H_{id}/n_1$, that is $\Delta H_a > \Delta H_w$ (or $\Delta H_a > Q\Delta H_{id}/n_1$) then the variation of $\Delta H_{id_{aq}}$ with solute concentration (*c*) will be similar in shape to Fig. 10 and is shown in Fig. 11. On the other hand if $\Delta H_a < \Delta H_{id}/n_1$, that is $\Delta H_a < \Delta H_w$ (or $\Delta H_a < Q\Delta H_{id}/n_1$), then the term $\Delta H_a - \Delta H_{id}/n_1$, in eqn (4) is positive and the expected variation of $\Delta H_{id_{aq}}$ with solute concentration is shown schematically in Fig. 12. Comparison of Figs. 10 and 11 (which represent eqns (7) and (4) respectively) shows that unfortunately the above theory does not allow a distinction to be made between (a) the adsorption of solute on top of adsorbed water and (b) the competitive adsorption of solute and solvent with $\Delta H_a > \Delta H_{id}/n_1$.

Although titanium dioxide pigments are subject flocculation and deflocculation phenomena it was thought that heat changes associated with flocculation were too small to be detected in the experiments reported here. If the heat change due to flocculation arises from the loss of kinetic energy due to Brownian motion and if about $5kT$ is lost each time a pigment particle enters a floc then for the pigment used the energy change would be about 10^{-6} J g^{-1} which would not be detected.

In the present work most of the solutes were surface active and in the concentrations used micelles would certainly be present. We would expect that thermal effects due to *changes* in micelles arising from adsorption of solute would be small since the amount of adsorbed solute is small compared with that in the bulk of the solution. In other words, the thermal effect of *displacement* in the micelle equilibrium resulting from adsorption of monomeric solute molecules or ions onto the pigment should be negligible. For the most concentrated solutions, however, the adsorption on the solid of whole micelles is an additional possibility. The shape of the $\Delta H_{id_{aq}}$ against concentration curve in this case is difficult to predict and is probably not justified for our experimental data.

The heats of immersion of the rutile were all greater in the solutions studied than in water. The heat of immersion curves for the various systems (Figs. 1–9) are not all identical which is probably due to the different values of ΔH_a for the solutes and their different extents of adsorption. The curves for potassium propionate, potassium octoate, sodium benzene sulphonate and potassium stearate (Figs. 1–4) probably all belong to the same class although the curve for potassium propionate (Fig. 1) indicates incomplete adsorption of the propionate ion whereas for potassium octoate, sodium benzene sulphonate and potassium stearate the curves suggest complete coverage of the pigment by the solute within the concentration range studied.

The heats of immersion in propionic acid solution and potassium oleate solution increase very rapidly with increasing solute concentration (Figs. 5 and 6). The propionic acid will very likely react chemically as well as physically with the coating of the amphoteric oxides on the surface of the rutile and thus give a fairly high exothermic reaction. (The reaction of the pigment with NaOH was even more exothermic but the results were not recorded accurately and are not reported here).

In the case of potassium oleate the adsorption on to the pigment of the oleate ion via the double bond may well occur and hence the heat of interaction of the ion with the solid is correspondingly different from that for KOct and KSt.

Although the curve for cetyl trimethyl ammonium bromide (Fig. 7) slightly resembles that for potassium propionate (Fig. 1) the resemblance may well be fortuitous since the solutes are so different. The cetyl trimethyl ammonium bromide is a highly active cationic surfactant and one would anticipate strong adsorption of the cation. An alternative explanation for the potassium propionate could of course be adsorption of the potassium ion on the pigment in preference to propionate ion and hence the resemblance of Figs. 1 and 7. The rheological behaviour of the pigment dispersions in these systems, however, was rather different and hence not too much emphasis should be placed on the slight similarity of the heat of immersion curves.

The heat of immersion of rutile in sodium lauryl sulphonate solutions (Fig. 8) appears to be constant within experimental error and independant of concentration in the range studied. Rheologically there were some similarities between the proprionic acid, cetyl trimethyl ammonium bromide and sodium lauryl sulphonate systems for rutile (to be reported) but the thermal behaviour of rutile in sodium lauryl sulphonate solution is unusual and involves rather a small heat of interaction.

The heat of immersion for the ethyl alcohol system (Fig. 9) shows the heat change to be close to that for water itself. This may be due *either* to the interaction of the OH group of the alcohol with the pigment being very similar to that of water, *or* alternatively very little of the alcohol is adsorbed.

Clearly the results indicate that for the systems studied the behaviour is not that described by eqns (4) and (6) with $\Delta H_a < \Delta H_{id}/n_1$ or $\Delta H_a < Q\Delta H_{id}/n_1$, (Fig. 12). Unfortunately it is not possible from the results to decide for the systems used whether adsorption of solute occurs on top of a full complement of water or if solute is adsorbed directly on the pigment in competition with water with the condition $\Delta H_a > \Delta H_{id}/n_1$ (or $\Delta H_a > Q\Delta H_{id}/n_1$). Intuitively, one might expect adsorption to take place on top of adsorbed water due to the strong affinity of the coated rutile pigment for water (Table 1), and hence eqn (7) would then be the appropriate equation for the rutile used.

REFERENCES

1 J. J. Cheswick and A. C. Zettlermoyer, *Advan. Catal.*, 11 (1959) 263.
2 J. G. Dawber, L. B. Guest and R. Lambourne, *Thermochim. Acta*, 4 (1972) 471.
3 W. D. Harkins, *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952.
4 A. C. Zettlemoyer, G. J. Young, J. J. Cheswick and F. H. Healey, *J. Phys. Chem.*, 57 (1953) 650.
5 J. J. Cheswick, A. C. Zettlemoyer, F. H. Healey and G. J. Young, *J. Phys. Chem.*, 58 (1954) 887.
6 J. J. Cheswick, A. C. Zettlemoyer, F. H. Healey and G. J. Young, *Can. J. Chem.*, 33 (1955) 251.
7 W. H. Wade and N. Hakerman, *J. Phys. Chem.*, 65 (1961) 1681.
8 T. Omori, J. Impai, N. Nahao and T. Morimoto, *Bull. Chem. Soc. Jap.*, 42 (1969) 943, 2198.