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# HEATS OF IMMERSION OF TITANIUM DIOXIDE PIGMENTS IN ALCOHOL–WATER MIXTURES

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## ABSTRACT

The heats of immersion of partially dried anatase and rutile pigments in mixtures of water with methanol, ethanol, and n-propanol were measured by a differential calorimetric method. The anatase heats of immersion could best be explained by assuming preferential adsorption of the alcohols, the effect being greatest for n-propanol. The rutile pigment, however, appeared to adsorb water preferentially in methanol–water and ethanol–water mixtures over the whole concentration range. In propanol–water mixtures the rutile pigment preferentially adsorbed water below an alcohol mol fraction of 0.25, and preferentially adsorbed propanol at mol fractions of alcohol greater than 0.25. The differences in behaviour between the two pigments may be explained qualitatively from the point of view of their surface morphology.

## 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 heat 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].

While the heats of immersion of titanium dioxide have been measured for a variety of systems[2–7], in all cases the samples of solid were thoroughly dried at temperatures up to 500°C and also outgassed at low pressures. Such treatment of commercial titanium dioxide pigments significantly impairs their usefulness as pigments, due to irreversible changes in their surfaces and the results obtained are not relevant in the industrial situation.

The purpose of the present work was to investigate the heats of immersion of two commercial, yet well characterised, titanium dioxide pigments; a coated rutile and an uncoated anatase. The coating on the rutile consisted of alumina, silica and zinc oxide. This amphoteric coating on the rutile improves its dispersibility in paints or printing-ink media and, in the case of paints, minimises the effects of the photo-initiated degradation of the resultant polymer film. Such surface coatings have been shown to be microporous by adsorption experiments[8]. Clearly, in the work described, where we refer to adsorption on "coated rutile", the dominant factor will be the amphoteric oxide surface and direct comparisons cannot be made with pure rutile.

In the work reported previously[9] the heats of immersion of partially dried and conditioned titanium dioxide pigments were measured in aqueous solutions of surfactant materials. In the present work the heats of immersion of partially dried anatase and coated rutile were measured in mixtures of water with methanol, ethanol and n-propanol over the whole range of concentration.

## EXPERIMENTAL

The calorimeter used in this work was of the differential type and its construction and method of operation have been described fully elsewhere[9]. The anatase and rutile pigments were those used previously. 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 water. The surface areas of the pigments were measured by nitrogen adsorption using a Strohlein area meter after they had been dried at 200°C in a stream of nitrogen for 3 hours. The values obtained were 9.0 $m^2\ g^{-1}$ for the anatase and 11.1 $m^2\ g^{-1}$ for the coated rutile. A full BET surface area determination on the rutile also gave a value of 11.1 $m^2\ g^{-1}$.

The water adsorbed on the pigments was measured by thermogravimetric analysis (TG) and also by Karl–Fischer titrations. The results are summarised in Table 1. The TG results showed that the rutile possessed more adsorbed water than the anatase and was much more difficult to remove. This may well be due to the porous nature of the coating on the rutile pigment.

TABLE 1

WATER CONTENT OF THE TITANIUM DIOXIDE PIGMENTS

| *Method* | *Water content (mg of $H_2O$ per g of pigment)* | |
|---|---|---|
| | *Anatase* | *Coated rutile* |
| (a) TG method | | |
| (i) 4 h at 140°C | 3.5 | 13.2 |
| (ii) 1.5 h at 550°C | 3.9 | 19.4 |
| (b) Karl–Fischer method | | |
| (i) dioxan solvent | 3.5 | 8.2 |
| (ii) methanol solvent | 3.4 | 11.8 |

For all the measurements reported here, both pigments were dried at 140°C and atmospheric pressure for several hours prior to use and are referred to as dried pigments ($S_d$) in spite of the fact that the rutile still possessed adsorbed water after this treatment. If an approximate molecular area of $10^{-19}$ m$^2$ is taken for the water molecule, then the conditioned anatase would possess approximately a monolayer of adsorbed water and the conditioned rutile would possess the equivalent of approximately six molecular layers of water. After drying at 140°C for several hours the anatase may be regarded as having been dehydrated while the rutile may be regarded as still possessing approximately two molecular layers of adsorbed water.

The methanol, ethanol and n-propanol were all of Analar Reagent quality. For measurements in the pure alcohols the liquids were pre-dried with molecular sieve 3A and then by the Grignard method. To avoid contamination of the pure alcohols during equilibration in the calorimeter they were stored with a small amount of molecular sieve 3A prior to immersion of the pigment samples. Mixtures of the alcohols with water were made up by weight to give known mol fractions of each component.

## RESULTS AND DISCUSSION

The heats of immersion $\Delta H_{id}$ of the dried anatase and rutile pigments in various alcohol–water mixtures are plotted in Figs. 1 and 2. The values of heat of immersion of the two pigments in the pure alcohols are compared with the values in water in Table 2. The ratios of $\Delta H_{id}$ for the two pigments in the same liquid are compatible with the results of Chessick *et al.*[5] who found that relative heats of immersion for several solids were practically independent of the solid.

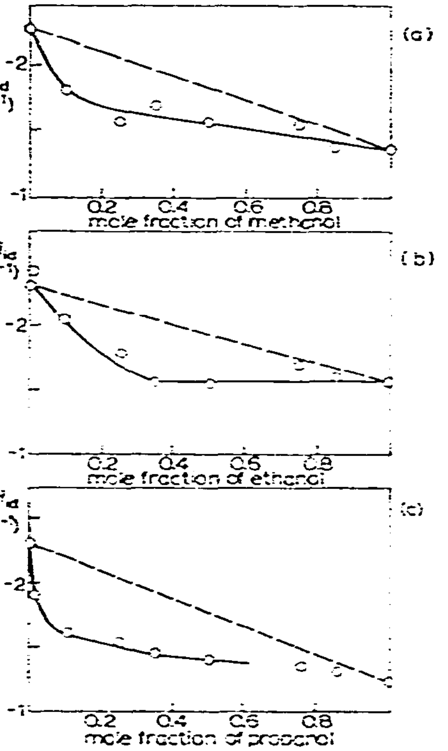
TABLE 2

HEATS OF IMMERSION OF TITANIUM DIOXIDE PIGMENTS IN PURE LIQUIDS

| | $\Delta H_{id}$ (J g$^{-1}$) | | | |
|---|---|---|---|---|
| | *$H_2O$* | *methanol* | *ethanol* | *n-propanol* |
| Anatase | −2.30 | −1.35 | −1.55 | −1.20 |
| Rutile | −5.70 | −3.70 | −4.0 | −3.50 |
| Ratio of $\Delta H_{id}$ for rutile/anatase | 2.5 | 2.7 | 2.6 | 2.9 |

The heat of immersion curves of the anatase in the alcohol–water mixtures (Fig. 1) fall fairly quickly initially as the amount of alcohol in the solution is increased, although at alcohol mol fractions greater than 0.2 the change in $\Delta H_{id}$ is less dramatic. For the coated rutile, however, the curves for $\Delta H_{id}$ exhibit maxima at fairly low alcohol mol fractions. The height of these maxima was greatest for the rutile–methanol–water system.

As discussed above the dried anatase was effectively dehydrated. Thus when the dried anatase is immersed in water it would regain approximately one molecular water layer. The dried rutile (which possessed two molecular layers of water) on immersion in water would regain its full complement of adsorbed water of about six molecular



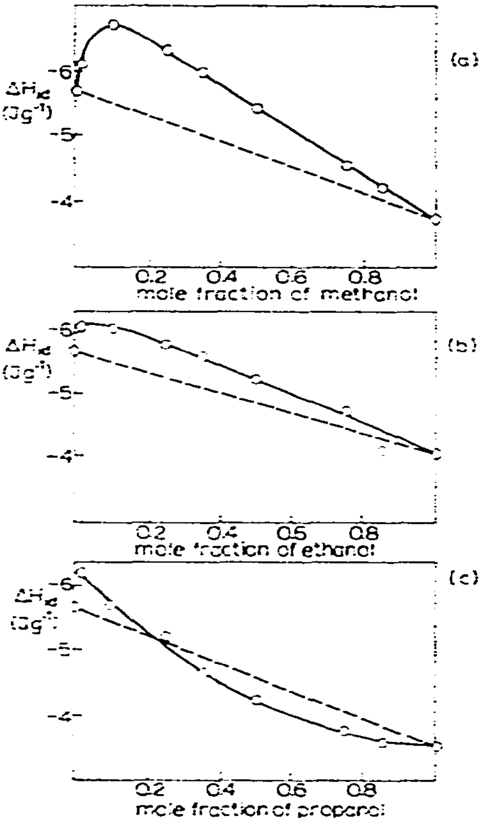


Fig. 1 (left). Heats of immersion of anatase pigment in (a) methanol–water, (b) ethanol–water and (c) n-propanol–water mixtures.

Fig. 2 (right). Heats of immersion of rutile pigment in (a) methanol–water, (b) ethanol–water and (c) n-propanol–water mixtures.

layers. In terms of mols of water this corresponds to $1.94 \times 10^{-4}$ mol $g^{-1}$ for the anatase and $7.3 \times 10^{-4}$ mol $g^{-1}$ for the rutile. From studies of adsorption of simple alcohols on dehydroxylated and partially dehydroxylated rutile[10] and also on polystyrene latex particles[11] it has been estimated that the alcohols are adsorbed to an extent of approximately 3 groups per $nm^2$ corresponding to an area available per alcohol molecule of about $3 \times 10^{-19}$ $m^2$. If we assume the same molecular areas for the alcohols in this work then this would correspond to $4.49 \times 10^{-5}$ mol $g^{-1}$ of alcohol for the anatase and $5.53 \times 10^{-5}$ mol $g^{-1}$ of alcohol for the rutile. These amounts of alcohol are much less than the corresponding amounts of water and therefore, it is perhaps not surprising that the heats of immersion of the pigments in the three alcohols are lower than those in water.

The relation between heats of immersion of dry solid and conditioned solid in a pure liquid is given by[9]

$$\Delta H^{\circ}_{id} - \Delta H^{\circ}_{ic} = \Delta H_{sv} - nL_v \qquad (1)$$

where $\Delta H^\circ_{id}$ is the heat of immersion of dry solid in a pure liquid, $\Delta H^\circ_{ic}$ is the heat of immersion in the pure liquid of the solid which has been conditioned in the vapour of the liquid, $\Delta H_{sv}$ is the heat of adsorption (or energy of adhesion) of $n$ mol of liquid on to the pigment, and $L_v$ is the molar heat of vaporisation. $L_v$ is counted as exothermic since the term arises from condensation of vapour. The difference $\Delta H_{sv} - nL_v$ is often called the *net integral heat of adsorption*. $\Delta H^\circ_{ic}$ would correspond to heat of immersion of solid conditioned by the alcohol vapour, namely the heat change for the process

$$\begin{array}{ccc} S_c & +l & \rightarrow S_l \\ (H_s) & (H_l) & (H_{sl}) \end{array}$$

so that $\Delta H^\circ_{ic} = H_{sl} - H_{sc} - H_l$. This process consists of replacement of the solid–vapour interface by the solid–liquid interface. The change in enthalpy per unit surface area accompanying production of this new interface is usually represented by an equation of the Gibbs–Helmholtz type

$$\Delta H = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_v$$

where $\gamma$ is surface free energy of the liquid and we will use this value for $\Delta H^\circ_{ic}$ in eqn (1). Thus for a pigment of surface area $A$ eqn (1) becomes

$$\Delta H^\circ_{id} - A\left(\gamma - T\frac{\partial \gamma}{\partial T}\right) = \Delta H_{sv} - nL_v. \tag{2}$$

If one assumes that the surface population of alcohol groups, when the pigments are immersed in pure alcohols, is the same as that reported by Jackson and Parfitt[10] and Ottewill and Vincent[11], namely 3 groups per nm$^2$ then $n$ can be calculated. For the anatase pigment in the three alcohols $A(\gamma - T(\partial\gamma/\partial T))$ was 0.42 J g$^{-1}$ whereas the corresponding value for the rutile was 0.52 J g$^{-1}$. Thus the heat of adsorption (adhesion energy), $\Delta H_{sv}$, may be calculated for the three alcohols on the anatase and the coated rutile. The calculated values of $\Delta H_{sv}$ are shown in Table 3. The molar energy of adhesion of water (physically adsorbed) on both pigments was found to be about −53 kJ mole$^{-1}$ per g of pigment. Thus the adhesional energies of methanol, ethanol and n-propanol are only slightly higher than that for water on anatase. For the coated rutile, however, the molar heats of adhesion of the alcohols are considerably higher than for physically adsorbed water. It has been suggested[10] that on *pure* rutile chemisorption of alcohols occurs and it would seem likely that chemisorption will also occur on the amphoteric oxide coating on the sample of rutile used in this work.

The heat of immersion of a solid in a mixture of two liquids is given by

$$\Delta H_{id} = x_1^a \Delta H^\circ_{id1} + x_2^a \Delta H^\circ_{id2} \tag{3}$$

where $x_1^a$ and $x_2^a$ represent the mol fractions of the components in the adsorbed surface layer, and $\Delta H^\circ_{id1}$ and $\Delta H^\circ_{id2}$ are the heats of immersion in the two pure liquids.

For a system in which neither of the two components is preferentially adsorbed on a solid, the graph of $\Delta H_{id}$ against mol fraction in the liquid phase would be expected to be linear.

TABLE 3

CALCULATION OF ENERGIES OF ADHESION ($\Delta H_{sv}$) FOR METHANOL, ETHANOL AND n-PROPANOL ON ANATASE AND RUTILE PIGMENTS

| *Alcohol* | $\Delta H_{dl}^{2}$ ($J\,g^{-1}$) | $n$ (*mole* $g^{-1}$) | $\Delta H_{sv}$ ($J\,g^{-1}$) | $\Delta H_{sv}$ (*kJ* $mol^{-1}$ *per g pigment*) |
|---|---|---|---|---|
| Rutile | | | | |
| methanol | −3.70 | $5.53 \times 10^{-5}$ | −5.12 | −93 |
| ethanol | −4.00 | $5.53 \times 10^{-5}$ | −5.58 | −101 |
| n-propanol | −3.50 | $5.53 \times 10^{-5}$ | −5.18 | −94 |
| Anatase | | | | |
| methanol | −1.35 | $4.49 \times 10^{-5}$ | −2.51 | −56 |
| ethanol | −1.55 | $4.49 \times 10^{-5}$ | −2.84 | −63 |
| n-propanol | −1.20 | $4.49 \times 10^{-5}$ | −2.57 | −57 |

The heat of immersion curves for anatase (Fig. 1) are considerably curved at low mol fractions of alcohol and indicate preferential adsorption of the alcohols on anatase. This is the most pronounced for solutions of propanol and this is consistent with the surface activity of this solute being greater in water than for solutions of methanol and ethanol.

The heat of immersion graphs for rutile in the methanol–water and ethanol–water systems (Figs. 2a and 2b) indicate preferential adsorption of water over the whole concentration range. For rutile in propanol–water mixtures, however, there appears to be preferential adsorption of water at propanol mol fractions less than about 0.25, whereas preferential adsorption of propanol occurs when its mol fraction in the liquid phase is greater than 0.25. Again this would be consistent with the greater surface activity of propanol solutions compared with methanol and ethanol solutions.

The peaks observed in the graphs of $\Delta H_{id}$ for the coated rutile can best be interpreted if a full complement of water is first adsorbed (about four molecular layers) followed by adsorption of alcohol on top of the adsorbed water. One possibility is that since the amphoteric coating on the rutile is fairly porous, some of the water is adsorbed in the pores and the remainder adsorbed on the surface along with the alcohol. As the alcohol concentration is increased and more alcohol is adsorbed, the driving force for adsorption of water decreases. Less water is then adsorbed in the pores and the total heat change starts to decrease as the concentration of alcohol is increased. The positions of the peaks for the three alcohols are at mol fractions of 0.12, 0.04, and 0.03 (approx.) for methanol, ethanol and propanol respectively.

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