
THE ADSORPTION OF A CATIONIC SURFACTANT ON TiO_2 FROM AQUEOUS SOLUTIONS¹

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ABSTRACT

Surface-tension measurements by the DuNuoy tensiometer technique have been used to estimate the number and size of rubber latex particles in aqueous suspension. The present report demonstrates the applicability of the bubble-pressure method to measuring the surface tension variation of solid aqueous suspensions on additions of a cationic surfactant. A consistent relationship between the specific surface area of the titania samples and surfactant adsorption is shown.

This paper describes a surface-tension method for estimating the adsorption of a cationic surfactant on titanium dioxide powders in aqueous suspension. The objective is to demonstrate the applicability of this method in showing a correlation between the amount of adsorption and the specific surface area of the solids used. Maron (1954) and his coworkers have used surface-tension titration techniques with potassium oleate and a du Nuoy tensiometer to estimate the amount of soap adsorbed on rubber latex emulsion particles. Their procedure for estimating the amount of soap adsorbed was based on the assumption that the difference in soap critical micelle concentration observed in water and a given weight of latex was the amount of soap adsorbed. The procedure described here is essentially the same, but employs a bubble-pressure method, a cationic adsorbent, and solid particles in suspension.

The surfactant is a pure grade of dodecyl dimethyl benzyl ammonium chloride (DDBA) obtained from Eastman Kodak Corp. This substance lowers the surface tension of water, and a plot of the logarithm of the surface tension against the concentration of DDBA is linear up to the critical micelle concentration

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(CMC). The same kind of plots result when the surface tension values of suspensions containing titania powders are plotted against the concentration of DDBA. The slopes of the linear portions are somewhat less than those obtained when the titration is made with pure water. The apparent CMC values thus obtained increase as the sample weight of the solid in suspension is increased. The difference in CMC value obtained with a given weight of titania and in water alone is assumed to be equal to the amount of DDBA adsorbed by the given weight of titania used.

A maximum-bubble-pressure technique was used to measure surface tensions. A large filtration flask is fitted with a two-hole stopper, in which are fixed a reservoir of butyl phthalate and tubing communicating to a narrow U-shaped water manometer. The side arm of the flask is connected by tubing to a thin-walled capillary with a polished tip. The latter is fixed at a known depth below the 50-milliliter level of a suspension contained in a small cylindrical vessel. The capillary is placed in a constant-temperature bath at 25°C. Bubbles of air are forced through the capillary at a rate of about six bubbles per minute from the capillary tip. After adding DDBA solution in one-milliliter increments, the

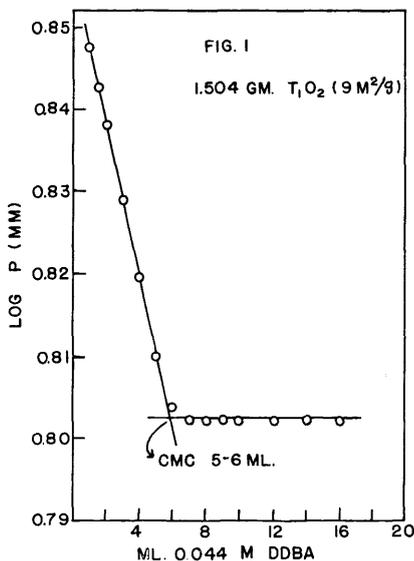


Figure 1. Typical plot of surface tension data for aqueous titania suspensions.

mixture is stirred, and then differences in level of the manometer legs are observed with a bench microscope. It is usually necessary to wait several minutes to attain a constant reading, which is recorded in mm of manometer-level difference. It is assumed that this difference is proportional to surface tension, so that, for the present purpose, the actual surface tensions need not be calculated.

A typical plot of $\log p$ (mm) against milliliters of DDBA solution is shown in figure 1. The CMC value is obtained from the plot by extrapolating the linear branches to a point of intersection. The final volume of the suspension is the sum of the original 50 milliliters plus the added DDBA solution. The CMC end point in milliliters is then converted to the actual molar CMC value by multiplying the molarity of the DDBA solution by the milliliters' end point, and by the final volume of the suspension, and then dividing by 1000. The concentration of the DDBA solution was found by potentiometric titration with 0.02 N silver nitrate to be 0.050 M. However, note that the plot in figure 1 was obtained with a 0.044 M solution.

Figure 2 shows a plot obtained when the CMC end points, in terms of milliliters of the DDBA solution, are plotted against the sample weights of a given titania powder. The slopes of these plots reflect the concentration of DDBA adsorbed per gram of solid. The values for slopes and intercepts were calculated

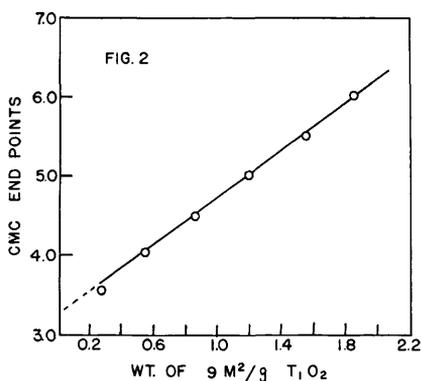


FIGURE 2. The linear variation of critical micelle concentration with weights of titania samples.

by the method of least squares and are recorded in table 1.

Three different titanias were used in this work, for each of which the BET areas were determined by the low-temperature nitrogen-adsorption method (Brunauer et al., 1938). The specific surface areas should be precise to better than 0.5 m²/g.

TABLE 1

TiO ₂	BET area	Intcpts.	slope ml/g	no./sq. m μ
Rutile	9 m ² /g	3.33 ml	1.42	0.79
Anatase	12 m ² /g	3.40 ml	1.72	0.72
Rutile	16 m ² /g	3.34 ml	2.21	0.72
		3.34 (H ₂ O)		

The slopes of plots like figure 2 are given in terms of milliliters corresponding to CMC end points. One may calculate the number of DDBA cations adsorbed per sq. m μ from the expression,

$$\frac{\text{slope (ml/g)} \times \text{CMC (moles/L)} \times 10^{-3} \text{ (L/ml)} \times 6 \times 10^{23} \text{ /mole}}{\text{BET area (m}^2\text{/g)} \times 10^{18} \text{ sq. m}\mu\text{/m}^2}$$

The CMC value in the numerator is the average calculated from extrapolated intercepts from plots at 0.00840 moles/L on figure 2.

The calculated values for each titania are in fair agreement, which show that the adsorption of DDBA is in direct proportion to the total area of the suspended solid. The results also suggest that the cross-sectional area occupied by a DDBA cation on the solid surface is about 130 sq. m μ , which is reasonable for a large cation like DDBA; but the procedure given here does not necessarily prove that DDBA cations are close packed on the solid surface. The active sites on titania which attract the cations are probably derived from negative charges on the titania surface.

REFERENCES

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