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From the AKZO Research Laboratories, Corporate Research Department Arnhem, (The Netherlands)

### The determination of contact angles of aqueous surfactant solutions on powders

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With 9 figures and 1 table

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Measurements of advancing contact angles for sessile drops on solid plates have frequently been reported in the literature (1-4). However, wetting of powders has only been studied sporadically (5, 6).

Using the *Washburn* equation for the flow of a liquid through a capillary it is possible to calculate from the rate of penetration the magnitude of the advancing contact angle and the work of adhesion between the liquid and the powder.

The results are of interest in the fields of adhesives technology, paints, printing inks and wetting of fabrics.

#### Theory

When a liquid penetrates a single capillary of radius  $r$ , the length of flow  $l$  in time  $t$  is given by the *Washburn* equation (7, 8).

$$l^2 = \frac{\gamma r t \cos \theta}{2\eta} \quad [1]$$

where

- $l$  length of flow in time  $t$ ,
- $\gamma$  surface tension of the liquid,
- $r$  radius of capillary,
- $\theta$  advancing contact angle,
- $\eta$  viscosity of the liquid.

The driving force for liquid penetration is governed by the pressure gradient  $\Delta P$  across the curved liquid interface. Therefore the liquid enters the capillary only spontaneously if the contact angle is less than  $90^\circ$ , so

$$\Delta P = \frac{2\gamma \cos \theta}{r} \quad (\text{Laplace}) \quad [2]$$

where  $r$  is the radius of the circular capillary.

A powder packed into a tube may be considered to consist of a bundle of capillaries of mean radius  $\bar{r}$ . Applying the *Washburn* equation to this system yields

$$l^2 = \frac{(c\bar{r}) \gamma t \cos \theta}{2\eta} \quad [3]$$

where  $c$  is a constant introduced to allow for the randomly oriented capillaries. For a given packing of the powder ( $c\bar{r}$ ) will be constant. Consequently there is a quadratic relationship between  $l$  and  $t$ , which depends only on the nature of the liquid. The value of ( $c\bar{r}$ ) can be calculated if a liquid is chosen for which  $\theta = 0^\circ$  (complete wetting or spreading).

Thus for other liquids both  $\theta$  and the work of adhesion  $W_a = \gamma(1 + \cos \theta)$  (solid saturated with vapour of the wetting liquid) can be calculated.

#### Experimental

##### Powders

Polyethylene terephthalate (PETP) and polyamide (nylon 11) powder were purified by extraction with water and petroleum ether. The nylon 11 powder was obtained from Aquitaine Organico, France. The graphite samples were used as received (Vos & Co., Amsterdam) and had a purity of 99.4-99.6%. Their particle size was less than  $33 \mu$ .

The aluminium powder, obtained from Pharmaceutische Groothandel ACF, Amsterdam, had a purity of more than 99% and was not further purified.

##### Organic liquids and surfactant solutions

All organic liquids were "Baker Analyzed" reagents. The sodium dodecyl sulphate (NaDS), obtained from BDH was a specially pure sample having a purity of at least 99%.

### Measurements

By manual tapping a known weight of powder was put in a glass tube, inner diameter about 0.8 cm. The tube was always filled to the same height in order to guarantee a constant packing density of the powder. The lower end of the tube was closed with a glass filter. The column was placed vertically in the wetting liquid and the time at which wetting started was observed (fig. 1). By means of a lamp the position of the liquid level could be read. Prewetting of the tube with the liquid and drying before packing facilitated the rise of liquid at the wall of the tube. All experiments were performed at 22 °C.

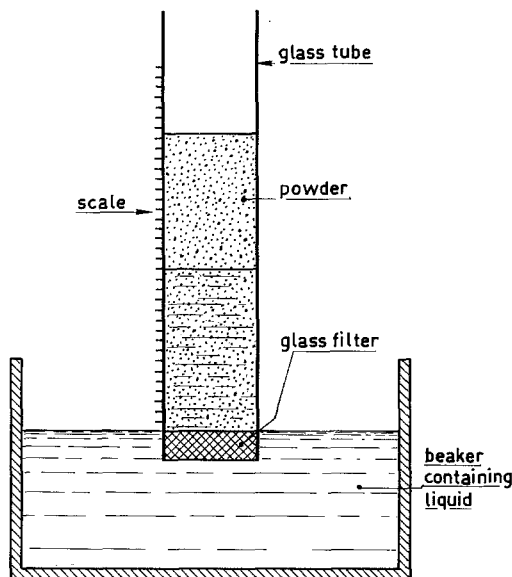


Fig. 1. Experimental setup for studying the wetting of powders

### Results

In all cases, except for the PETP, linear plots of  $l^2/t$  were obtained, which indicates that the effect of gravity can be neglected and that the physical structure or porosity of the powders is constant throughout the wetting process. In the PETP-NaDS system, at low surfactant concentration, there might be some adsorption of surfactant ions on the polyester surface. However, the calculated contact angles and the corresponding adhesion energies are based upon the slope at the very first beginning of the curves (fig. 5).

From the slopes of the lines, the viscosities, the surface tensions of the liquids and the surfactant solutions, values of  $(c\bar{r} \cos \theta)$  (eq. [3]) have been calculated [the values of the surface tensions of the NaDS solutions were taken from ref. (9)]. For the aluminium powder it has appeared that benzene yields the maximum value of  $(c\bar{r} \cos \theta)$  out of a series of ten liquids. So the contact angle of

benzene on aluminium powder is put equal to zero. Since there is no very clear relation between the contact angle and the molecular structure of the wetting liquids (see table 1), it might be that there are other liquids, not studied, that wet aluminium still better than benzene. This may be considered a drawback of the method.

Table 1. Contact angle and adhesion energy of some liquids on aluminium powder

Liquid	$\theta$ (°)	$W_a$ (erg/cm <sup>2</sup> )
Benzene	0	58
<i>n</i> -Hexane	14	36
Toluene	20	55
<i>n</i> -Heptane	25	39
Chloroform	26	52
Acetone	27	45
DMF	35	68
Ethanol	41	40
Methanol	46	38
Water	48	121

The contact angles for the other liquids can now easily be calculated. Also the work of adhesion,  $W_a = \gamma(1 + \cos \theta)$ , can be calculated.

For sake of clarity not all experimentally obtained straight lines are plotted, fig. 2. The liquids used and their corresponding  $\theta$  and  $W_a$  values are summarized in table 1.

Also the wetting properties of aqueous NaDS solutions on aluminium have been studied. The surfactant concentrations ranged from about 0.001 molar to 0.04 molar, thus covering the critical micelle concentration (c.m.c. = 0.008 molar), fig. 3. The calculated  $\theta$  and  $W_a$  are plotted in fig. 4.

The same procedure was applied to PETP, nylon 11 and graphite powders. The calculated values of the resulting contact angles and the corresponding adhesion energies are plotted in figs. 6–8. For the purpose of clarity not all  $l^2/t$  lines have been plotted for the PETP-NaDS system (fig. 5); for nylon 11 and graphite powders only the contact angles and the adhesion energies involved have been plotted.

### Discussion

From the plots of the contact angles vs. the surface tension of the aqueous NaDS solutions some general trends emerge:

1. The contact angle decreases with increasing surfactant concentration (lower surface tension). The same holds for the adhesion energy.

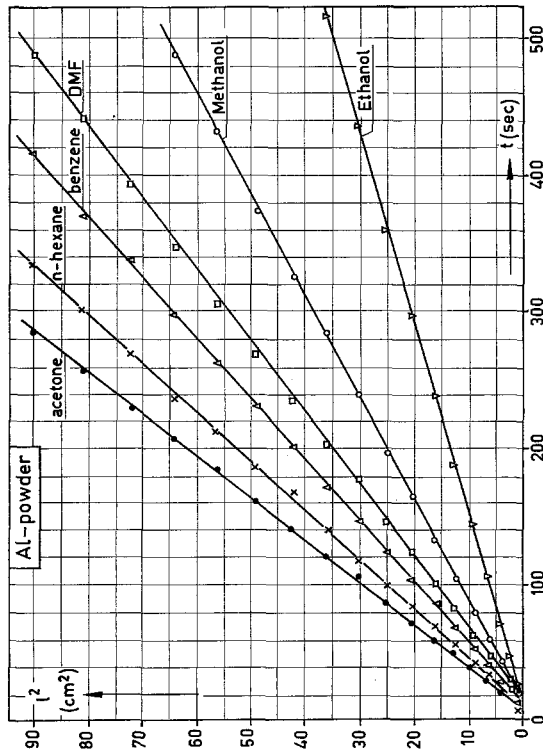


Fig. 2. Wetting of aluminum powder by different liquids

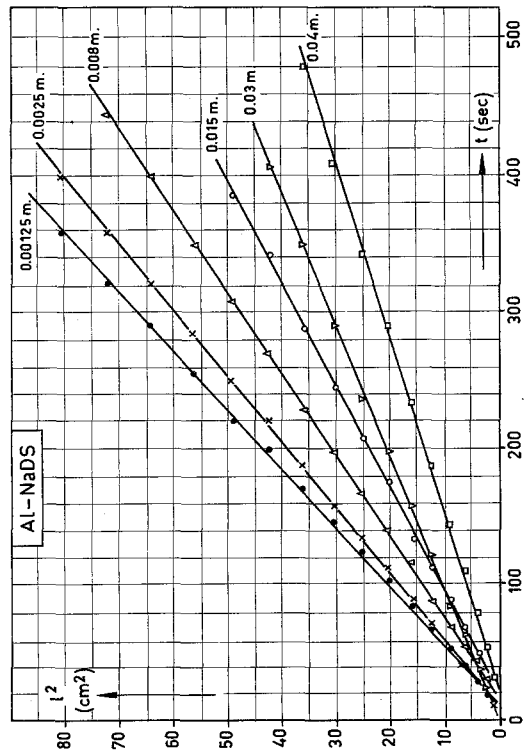


Fig. 3. Wetting of aluminum powder by sodium dodecyl sulphate solutions

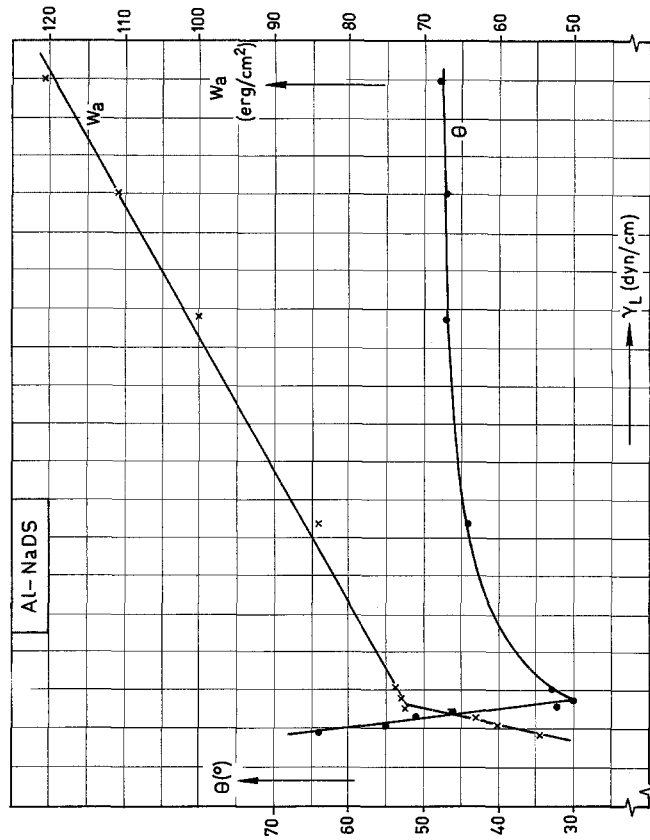


Fig. 4. Contact angle and adhesion energy for the system aluminum-NaDS. Influence of the surface tension of the NaDS solution

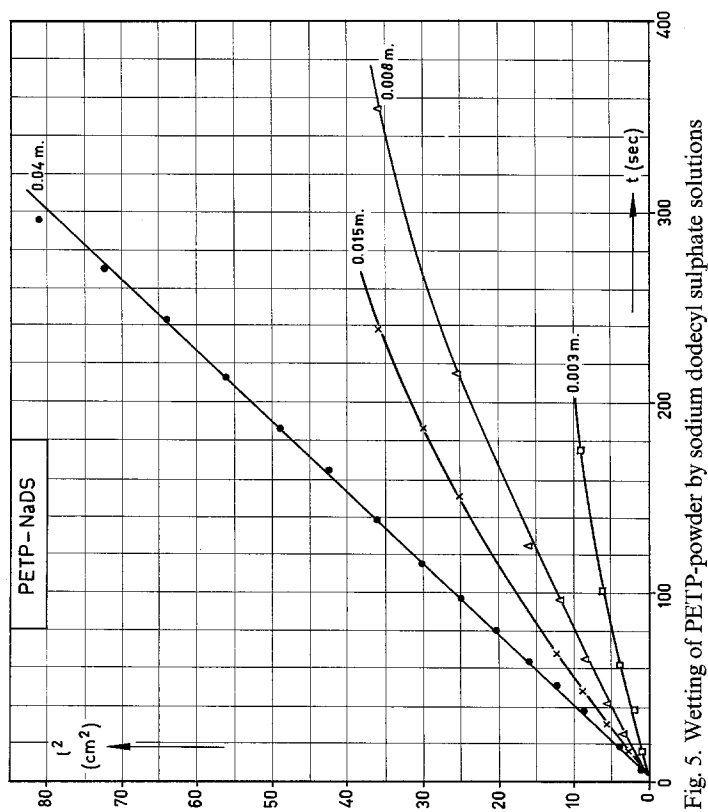


Fig. 5. Wetting of PETP-powder by sodium dodecyl sulphate solutions

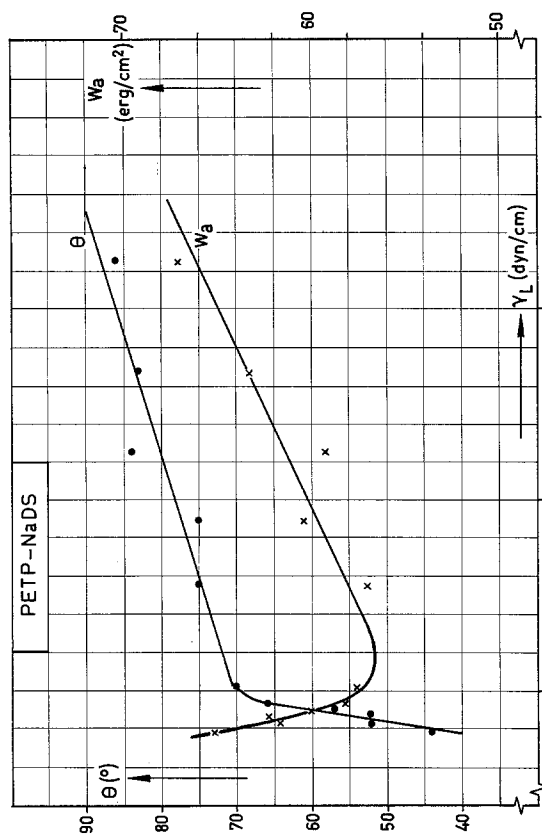


Fig. 6. Contact angle and adhesion energy for the system PETP-NaDS. Influence of the surface tension of the NaDS solution

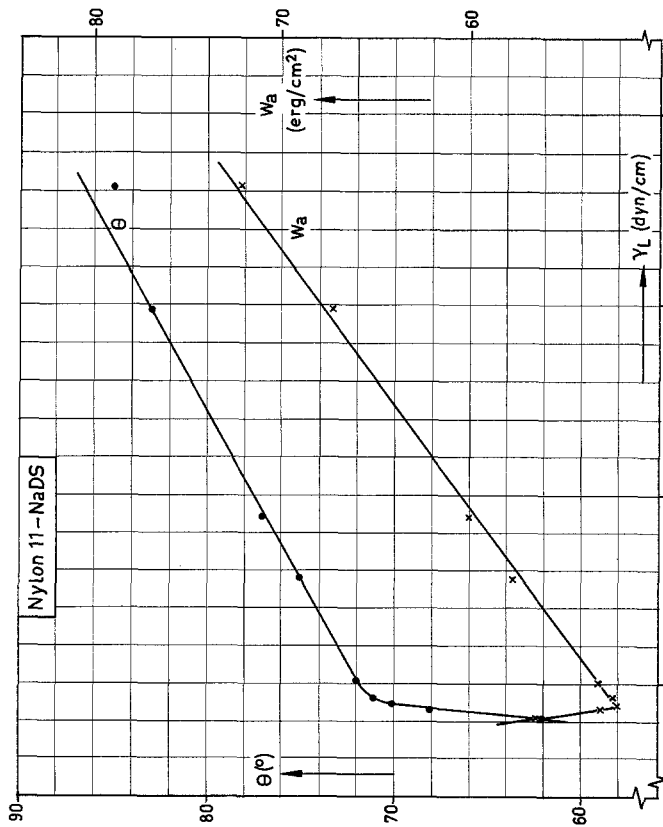


Fig. 7. Contact angle and adhesion energy for the system nylon 11-NaDS. Influence of the surface tension of the NaDS solution

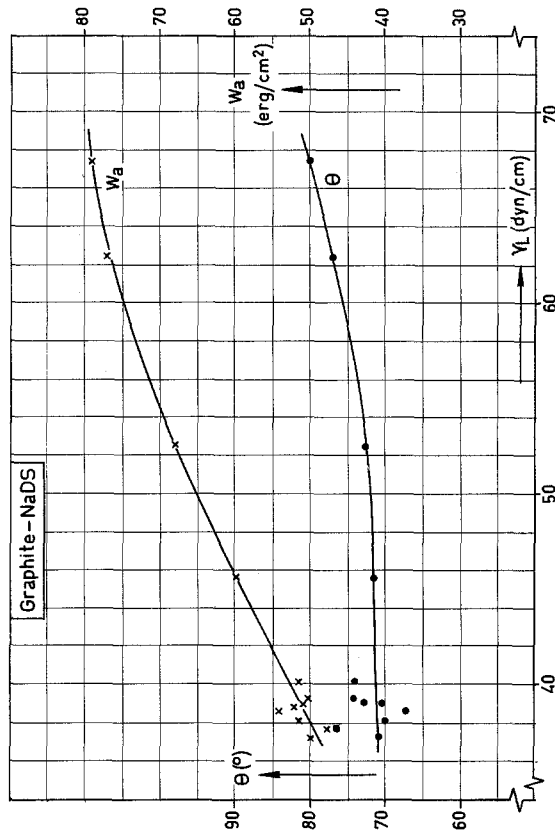


Fig. 8. Contact angle and adhesion energy for the system graphite-NaDS. Influence of the surface tension of the NaDS solution

2. All curves show an abrupt change of the contact angle, and consequently of the adhesion energy, close to the critical concentration of micelle formation ( $\gamma$  is 39 dyn/cm), except for the graphite-NaDS system.

3. The contact angles on the low-energy polymers are larger than on aluminium. In terms of contact angles, graphite might be classified as a polymer.

With respect to the wetting behaviour of the surfactants on the polyester and polyamide powders the same trends were observed as found by other authors (1, 2), who used plates instead of powders. However, quantitative comparison of the contact angles obtained by the "powder" method on the one hand and by the "plate" method on the other is not allowed, because recent studies (10) have revealed that the contact angle on plates is somewhat dependent on the drop size.

On the basis of the results the following mechanism of the wetting process of the different substrates by aqueous NaDS solutions can be put forward (fig. 9).

### PETP and NYLON II

At surfactant concentrations below the c.m.c. the relatively hydrophobic surfaces of these polymers are occupied by the surfactant ions  $C_{12}H_{25}SO_4^{\ominus}$  ( $\sim 0$ ) as schematically represented in fig. 9. The paraffin chains adhere to the polymer surface and the contact angle decreases.

At the c.m.c. the surface is fully occupied by the surfactant ions and a closely packed monolayer is formed. In this stage the originally hydrophobic nature of the polymer surface has become hydrophilic (hydrated dodecyl sulphate ions).

At surfactant concentrations above the c.m.c., wetting by the aqueous solution is drastically facilitated:  $\theta$  decreases abruptly and a second layer of surfactant ions is built upon the first layer.

### Aluminium

This hydrophilic, polar substrate is wetted by the surfactant solution in the following way (fig. 9). At surfactant concentrations below the c.m.c. the ions are adsorbed with their sulphate head groups on the surface.

At the c.m.c. a closed monolayer is formed. The surface has become paraffinic and hydrophobic in nature.

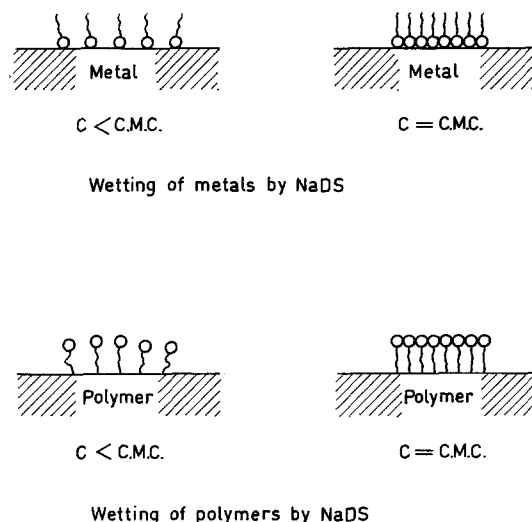


Fig. 9. Schematic representation of the wetting of metals and polymers by aqueous sodium dodecyl sulphate solutions

At surfactant concentrations above the c.m.c. the surfactant ions adhere to the first layer, thus forming more or less a bimolecular layer. Because of the low energy and the hydrophobic nature of the first layer, wetting is more difficult and the contact angle becomes larger.

This picture is less pronounced for the graphite system.

### Summary

The wetting behaviour of aqueous sodium dodecyl sulphate solutions on polyester, polyamide, aluminium and graphite powders has been studied.

The method described is based on the unopposed penetration of the liquid into a plug of powder packed in a glass tube. Using the Washburn equation for the flow of a liquid through a capillary, it is possible to calculate from the rate of penetration the magnitude of the advancing contact angle and the work of adhesion between the liquid and the powder. The results show details as to the mechanism of adsorption of the surface-active molecules on polymer and metal surfaces.

### Zusammenfassung

Die Benetzung von wässrigen Natriumdodecylsulphatlösungen auf Polyester-, Polyamid-, Aluminium- und Graphitpulvern wurde studiert. Die Methode beruht auf dem spontanen Fließen der Flüssigkeit in einem mit dem Pulver gepackten Glasrohr. Mit Hilfe der Washburnschen Gleichung für das Fließen einer Flüssigkeit durch Kapillaren ist es möglich, aus der Durchdringungsgeschwindigkeit den Wert der fortschreitenden Kontaktwinkel und die Adhäsionsarbeit zwischen Flüssigkeit und Pulver zu berechnen.

Die Ergebnisse zeigen Einzelheiten hinsichtlich des Mechanismus der Adsorption von grenzflächenaktiven Molekülen an polymeren und metallischen Oberflächen.

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