On the Thermodynamics of Interfaces and Its Application to Detergency

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1. DETERGENCY

One of the fields in which interfacial phenomena play a great role in practice is detergency, for instance of clothes (laundrying) or of glass and porcelain (dish washing). In the production of detergents the problem arises to evaluate their efficiency, and this problem led to the following considerations.

There seems to be to some extent a general inclination to regard a surface tension-concentration curve combined with an analysis of the product for contents of "active" substance as a sufficient basis for an evaluation of the mentioned nature, the word surface being taken to mean the interface against air. The quantity which is essential to accomplish detergency must, however, be the mechanical work which must at the temperature of detergency and atmospheric pressure be done upon the system if the process is carried through reversibly. Perhaps this is expressing it rather schematically, but if we confine ourselves to consider dish washing (where the soil at detergency temperature can practically be considered liquid) *, such factors as the possible deleterious effect of the detergent on the object of detergency will not influence the evaluation, and the detergent permitting detergency to be carried out completely involving the smallest amount of work must be said to be best.

After these considerations it would be natural to resort to Dupré's expression for adhesion work.**

We shall consider a cylinder or other body built up of two phases 1 and 2, and surrounded by a third, 3 (Fig. 1). 3 may be a detergent, 2 fat, and 1 porce-

* This assumption is mentioned with a view to the following considerations.

** The writer has planned to discuss the use of this expression more in detail in another paper.

Fig. 1 A. Fig. 1 B.

lain. If 1 and 2 are separated, the interface 12 disappears, and new interfaces 13 and 23 appear. Using the terms γ for interfacial tension, σ for interfacial area with pertinent indices, and in putting $-d\sigma_{12} = d\sigma_{13} = d\sigma_{23} = 1$ and $W_A =$ adhesion work, we obtain according to a paper from 1869 by Dupré

$$W = -\gamma_{12} + \gamma_{13} + \gamma_{23} \quad (1)$$

For phase 1 = phase 2 we have specifically adhesion work = cohesion work = $2\gamma_{13}$ ($= 2\gamma_{23}$).

The use of the expression requires some comments as it will appear from the following. First it might, however, be said that in laundering, which takes longer time in practice than dish washing, the overcoming of adhesion is not the sole object, as in the former case redeposition of the soil must also be prevented. But dish washing will not allow time enough for redeposition phenomena to occur. The ideal case would be $W_A < 0$ as 1 and 2 would then be separated simply by being placed in the medium 3. In that case redeposition on the object of detergency would not occur. The important factor in evaluation would then be the time required for the process of separation.

If values for $-W_A$ are used as a measure of the "efficiency", difficulties are immediately encountered. The reason is that it is not surface tensions which are involved, but on the contrary interfacial tensions liquid-liquid and liquid-solid. Surface tensions and tensions liquid-liquid can be measured directly, but for tensions liquid-solid no general methods are stated in the literature. In the following it will be shown that at any rate in principle it will be possible to measure the quantity W_A .

2. ON THE POSSIBILITY IN PRINCIPLE TO MEASURE THE ADHESION WORK

Equation (1) includes the tensions in interface 13 and 12, where 1 is the solid phase; but they are included as a difference which it will be possible in principle to measure.

We shall consider a drop of 2 in equilibrium on a plane layer of 1. (Fig. 2). 1 and 2 are surrounded by 3. A virtual displacement during which the contact angle $= \Theta$ and the volume of the drop is kept constant (constant volume in order to avoid a spatial contribution to the work) gives at once the known condition of equilibrium stated by Young (1805)

$$\cos \Theta = \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}} \quad (2)$$

This relation can be used for our purpose. For the sake of clearness we shall designate

Phase 1 by P (porcelain)
 Phase 2 by O (oil)
 Phase 3 by D (detergent) or when phase 3 is
 gaseous Phase 3 by G (gas).

Furthermore, Θ_{ab}^c is the contact angle between phase a and phase b, a and b being surrounded by c.

(2) now gives the following relations for O-drops in equilibrium on plane P-layers:

$$\cos \Theta_{PO}^G = \frac{\gamma_{PG} - \gamma_{PO}}{\gamma_{OG}}$$

$$\cos \Theta_{PD}^G = \frac{\gamma_{PG} - \gamma_{PD}}{\gamma_{DG}}$$

whence we obtain if P has been surrounded by the same G-phase during the two determinations so that γ_{PG} is the same

$$\gamma_{PD} - \gamma_{PO} = \gamma_{OG} \cos \Theta_{PO}^G - \gamma_{DG} \cos \Theta_{PD}^G \quad (3)$$

With the new symbols (1) is written

$$W_A = -\gamma_{PO} + \gamma_{PD} + \gamma_{OD}$$

which combined with (3) gives

$$W_A = \gamma_{OG} \cos \Theta_{PO}^G - \gamma_{DG} \cos \Theta_{PD}^G + \gamma_{OD}$$

in which W_A is expressed by the contact angles for O and D-drops against plane P-layers and easily measurable tensions (liquid-liquid and liquid-gaseous).

C_1 and C_2 denoting measurable constants dependent on oil and detergent, respectively, and both dependent on porcelain, we can write

$$W_A = \gamma_{OG} C_1 - \gamma_{DG} C_2 + \gamma_{OD}$$

For a given oil and a given object of detergency it is thus possible to express the adhesion work by the surface tensions of oil and detergent and their interfacial tension and C_1 and C_2 .

From experience we know that the ordinary detergents wet glass and porcelain particularly well so that in general we shall have small values for Θ_{PD}^C . With approximation we shall thus be able to put $C_2 = 1$, and we then obtain

$$W_A = \gamma_{OG} C_{PO} - \gamma_{DG} + \gamma_{OD} \quad (4)$$

C_1 being designated C_{PO} because it is dependent on the natures of O and P.

It is hardly feasible to eliminate C_{PO} from the expression, as this would indicate that all kinds of oil and porcelain (and glass) were having the same contact angle against gas (air). In other words: If it is wanted to evaluate a detergent, W_A must be found for a number of representative kinds of O and P, which means that one figure for W_A will not suffice. This procedure would involve a differentiation between detergents suited for washing certain objects of detergency. The O-kinds may be considered fairly constant. If this latter assumption holds, (4) can be written

$$W_A = C_P - \gamma_{DG} + \gamma_{OD},$$

where C_P is a constant only dependent on the nature of the object of detergency. The members at disposal in (4) are at any rate γ_{DG} and γ_{OD} , which can be varied through choice of detergent and its concentration.

From the above it will be seen that it will be advantageous for the separation of P and O to choose γ_{DG} high (which is probably contrary to the most usual view in practice) * if at the same time γ_{OD} can be low. Here the problem arises whether there is any relationship between γ_{DG} and γ_{OD} or, more in general, between γ_{OG} , γ_{DG} and γ_{OD} . In that case W_A could be rewritten so that it contained only *surface* tensions. The question whether it is possible from the *surface* tensions of two liquids to compute their interfacial tension has occupied many research workers in the course of time. The assumption that such a relation exists is based by its supporters on a paper from 1907 by Antonoff¹.

This relation which is usually called Antonoff's rule will now be discussed.

* In practice there is a tendency to consider only the wetting of P and O, i. e. replacement of the surrounding gaseous phase by D, and making γ_{DG} only responsible for this process, which is not in the present paper regarded as any important problem.

3. ANTONOFF'S RULE

Antonoff's rule is as follows:

$$\gamma_{AB} = \gamma_A - \gamma_B \quad (5)$$

where γ_{AB} is the interfacial tension between the two liquids A and B with surface tensions γ_A and γ_B . From a formal viewpoint this seems immediately objectionable; for when $\gamma_{AB} = \gamma_A - \gamma_B$, we must have $\gamma_{BA} = \gamma_B - \gamma_A$, but γ_{AB} and γ_{BA} are identical quantities. In other words (5) is wanting in symmetry with respect to the way in which the surface tensions of the two liquids are included in the equation. For example the question can be put: Is $\gamma_{OD} = \gamma_{DG} - \gamma_{OG}$ or $\gamma_{OD} = \gamma_{OG} - \gamma_{DG}$?

In the former case (4) can be written

$$W_A = \gamma_{OG}(C_{PO} - 1), \quad (6)$$

which would be a convenient solution to the problem of evaluating detergents, as it would mean that they are all equally good and equally good in large concentration intervals (or practically equally good, equation (4) being based upon $\theta_{PD}^G \sim 0$).

As it is, however, known from experience that $\gamma_{DG} > \gamma_{OD}$ and $\gamma_{OG} > 0$, (6) must be a conclusion from Dupré's and Antonoff's expressions; for $-\gamma_{OG}$ must be negative, and the expression $\gamma_{OD} = \gamma_{OG} - \gamma_{DG}$ would give absurdly high values for γ_{OG} , viz. $\gamma_{OD} + \gamma_{DG}$. If for example D = water, the result would be obtained that the surface tension of oil were higher than that of water. This result is evidently inconsistent with experience*.

To the above it may at once be said that Antonoff states that his rule will only give correct results if certain conditions are met: Phase A must be saturated with B and vice versa. In other words the system must be in chemical equilibrium, and the mutual solubility may change the values inserted in (5) materially. We can illustrate this fact with an example. In the literature we find

$$\left. \begin{array}{ll} \gamma_{\text{water, air}} = 72.8 & \gamma_{\text{benzene, air}} = 28.9 \\ & \text{water, benzene} = 35.0 \end{array} \right\} \begin{array}{l} \text{measured in dynes/cm} \\ \text{at } 20^\circ \text{C.} \end{array}$$

But if we form $\gamma_{\text{water, air}} - \gamma_{\text{benzene, air}}$ we obtain $\gamma_{\text{water, air}} - \gamma_{\text{benzene, air}} = 43.9$, which is inconsistent with the measured value.

* As an example we have at 20°C

$$\begin{array}{ll} \gamma_{\text{water, air}} = 73 \text{ dynes/cm;} & \gamma_{\text{oleic acid, air}} = 32.5 \text{ dynes/cm;} \\ & \gamma_{\text{water, oleic acid}} = 15.6 \text{ dynes/cm.} \end{array}$$

Fig. 2

Fig. 3

Fig. 4

But Antonoff saturates water and benzene mutually, and for the aqueous solution A he finds ¹

$$\gamma_{AG} = 70.6 \text{ against air}$$

$$\gamma_{AG} = 60.0 \text{ against vapours}$$

and

$$\gamma_{BG} = 28.2 \text{ (B = "benzene phase")}$$

and the rule holds beautifully when we choose γ_{AG} against vapours.

On the basis of corresponding measurements for the systems *isobutyl*-alcohol-water, *isoamyl*alcohol-water, ether-water and chloroform-water Antonoff sets forth his rule as a general rule, on condition that regard is being had to establishment of equilibrium. For the system ether-water he even takes measurements at three temperatures: 14° C, 20° C, 24° C. But he omits to point out that the rule only holds at 14° C. This fact (in the opinion of the writer) invalidates the rule. A "rule" which holds only at a random temperature — or rather a temperature dependent on the system but not predictable — is no rule.

Finally, from a theoretical standpoint there is no reason why the rule should hold exactly at chemical equilibrium; for the conditions of equilibrium can never involve any relationship between the quantities included in (5). Let us consider a system consisting of a liquid phase A with a drop of B on the surface, all surrounded by a gaseous phase C (Fig. 3). With respect to the *mechanical* stability of the system we have the alternative: Either the drop represents a stable form of equilibrium, or stable mechanical equilibrium will not occur until B has spread over the surface AC. If in the latter case the drop is spreading in a layer of a certain thickness, the final result will be such a layer and B-surplus in drop form, *e.g.* monomolecular films ².

In the former case we can find the mechanical conditions of equilibrium by making virtual displacements corresponding to those mentioned in the description of Fig. 2. But illustrating the case more clearly, we shall obtain them by observing that γ_{AC} , γ_{CB} and γ_{AB} must form a closed polygon of forces (triangle of forces) as shown in Fig. 4, where γ_{AC} is designated γ_{AG} and

γ_{BC} is designated γ_{BG} , while $C = \text{gas (air)}$. It appears clearly that here γ_{AB} cannot be $= \gamma_{AG} - \gamma_{BG}$. By a calculation it is at once seen from the cosine relations, which give

$$\begin{aligned}\gamma_{AB}^2 &= \gamma_{AG}^2 + \gamma_{BG}^2 - 2 \gamma_{AG} \gamma_{BG} \cos \theta_1 \\ \gamma_{BG}^2 &= \gamma_{AB}^2 + \gamma_{AG}^2 - 2 \gamma_{AG} \gamma_{AB} \cos \theta_2\end{aligned}\quad (7)$$

whence by inserting $\gamma_{AB} = \gamma_{AG} - \gamma_{BG}$ we obtain

$$\begin{aligned}\cos \theta_1 &= 1 & \cos \theta_2 &= 1 \\ \theta_1 &= 0 & \theta_2 &= 0\end{aligned}$$

This means that the triangle and consequently the drop cannot exist in a stable form, which we assumed. Thus Antonoff's rule cannot hold in this case, and it should be noted, neither at chemical equilibrium nor at chemical non-equilibrium; for if the system begins in chemical non-equilibrium with a mechanically stable drop and ends in chemical and mechanical equilibrium with a drop, a triangle of forces must exist at the initial as well as the final states, it must be admitted with triangle sides varying from beginning to end.

(7) shows that γ_{AB} must in this case be higher than determined by Antonoff's rule.

If the other possibility occurs, *i.e.* that the drop is spreading, neither in that case will there be any reason why (5) should hold. For spreading does not require $\cos \theta_1 = 1$ and $\cos \theta_2 = 1$ as a necessary condition. The latter is only a specific case, and in this case Antonoff's rule will hold, but it can never be known beforehand whether this specific case is occurring. The condition for using the cosine relations was mechanical equilibrium with drop, and when the condition is not fulfilled, the cosine relations cannot be applied to the phenomenon.

Finally it should be mentioned that when we do not find higher but nearly always lower values for γ_{AB} than supposed by Antonoff's rule, it is due to the fact that as a rule the drop is not in equilibrium with the interface AC proper, but with a spread surface layer on the latter, and the surface layer is so thin that its tension is a special film tension and not γ_{AC} . This phenomenon is dealt with in detail by Harkins².

With regard to an application of Antonoff's rule to oil-detergent (particularly oil-pure water) solutions, the example mentioned in the footnote on p. 817 shows clearly that for non-equilibrium values it does not hold. Moreover, as the mutual solubility of oleic acid-water is very slight, it probably will not hold if the liquids are mutually saturated.

Fig. 5 A

Fig. 5 B

4. EVALUATION OF D BASED ON THE PRECEDING CONSIDERATIONS

In the detergency literature many examples are found of surface tension and interfacial tension-concentration curves, *e.g.* in Niven's book on the subject³. It appears that γ_{DG} and γ_{OD} curves for the various known detergents do not show great variations, and the possibilities of variation through the nature of detergents in accordance with (4), *i.e.* high γ_{DG} and low γ_{OD} do not seem as large as might have been expected.

Figures 5 a and b indicate a general course of such tension-concentration-curves*. It is, however, an open question whether these curves can be of any assistance in evaluating which concentration should be chosen. As Dupré's formula applies to reversible separation, it requires equilibrium values for the γ 's.

But if importance is attached to the curves on the assumption that mutual solubility is slight, it is interesting that in view of the preceding considerations concentration c'' , Fig. 5 a, should not be chosen for detergents having the represented course of the curve. c'' corresponds to the lowest surface tensions, and is consequently the concentration considered to be best in practice. As we should, however, have γ_{DG} as high and γ_{OD} as low as possible, c' must be chosen. However, c'' and c' are not very far apart; but it is also remarkable that the detergency curve in Fig. 14—2, page 232 in Niven's book³ reaches its maximum at c' after which it remains practically level, and that a major part of the steep increase of the curve occurs in the interval from c'' to c' .

* The writer has seen such tension-concentration curves verified by measurements against air with du Nöuy's tensiometer.

Fig. 6

Finally it is evident that if the values from such curves are required together with γ_{OG} against air to satisfy Antonoff's rule, the latter is invalidated, as $\gamma_{DG} - \gamma_{DO} = \gamma_{OG} = \text{constant}$ according to the rule.

With regard to the possibility of measuring the contact angle θ it is a condition that no phenomena of hysteresis occur for this angle, θ must have the same value when the drop of O or D is brought to a state of equilibrium by spreading and by contraction.

The actual measurement is easily carried out by microphotography of the drop from the side. Such measurements are often described in the literature, e.g. by Talmud and Lubman ⁴ for a drop surrounded by a liquid phase resting on a plane solid phase.

The writer has, however, tried a method which is not to be found in the literature, and which only requires a very simple apparatus.

With a Carlsberg pipette a small drop of known volume corresponding to that of the pipette is slowly blown on to a plane P layer which is placed horizontally. Such small drops (10–40 mm³) may with good approximation be considered spherical segments of one base. As we have one of the drop's geometric parameters, viz. volume *, only one more is required for determination of the configuration. For this purpose the maximum height above the P-layer was chosen. With a spherometer ** this height can be measured with the accuracy of a few per cent. The method only requires little time and cheap apparatus, but with regard to accuracy it is inferior to microphotography. It may, however, give better values than the «tilting plate-method», where a P-plate is tilted 90°—contact angle until the meniscus adjoins the latter-horizontally. h being the maximum height, v being volume of the drop, and θ being the contact angle sought (Fig. 6), we find

$$\cos \theta = \frac{v - 2/3\pi h^3}{v + 1/3\pi h^3} \quad (8)$$

* There is actually an additional pressure in a drop, but a calculation on the basis of the dimensions occurring in such measurements compared with the order of magnitude of the compressibility coefficients of liquids shows that the compression will have no measurable influence on volume.

** We get a very sharp indication that the screw of the spherometer touches the drop in that as soon as they touch, the drop changes its form and is spreading over the end of the screw.

For small Θ (small h), the members including h^3 will be insignificant compared to the v which can be produced with Carlsberg pipettes, and $\sin \Theta$ must be used in an approximated form. r being the radius in the base of the spherical segment of one base, we obtain

$$\sin \Theta = \frac{2rh}{r^2 + h^2}$$

and

$$r^2 = \frac{2v}{\pi h} - \frac{h^2}{3}$$

For small h the latter may be approximated

$$r^2 = \frac{2v}{\pi h}$$

and hence

$$\sin \Theta = \frac{\sqrt{2v\pi h^3}}{v + \frac{h^2}{2}} \quad (9)$$

which may again for very small h be approximated

$$\sin \Theta = \sqrt{\frac{2\pi h^3}{v}} \quad (10)$$

For an increasing contact angle equations (10), (9) and (8) are to be used successively.

The following can be stated as an example of such measurements:

Sheets of plate glass were cleaned by standing in a potassium dichromate-sulphuric acid solution for 24 hours, whereupon they were rinsed in tap water, distilled water, alcohol and ether in the succession mentioned.

Drops of distilled, boiled water were placed on the sheets with a Carlsberg pipette of 40 mm³.

Five experiments were made, at the beginning of each five drops were measured, and h varied in the interval $0.37 \text{ mm} \leq h \leq 0.40 \text{ mm}$. Thus it seems that we have here a well defined contact angle *. The measurements were made at 18°C–20°C and against air.

The sample sheets remained in the same room, and measurements on new drops were made regularly and frequently. In all cases the initial value proved to last only a few minutes, and h increased at a decreasing rate, until after

* This contact angle is not given, because correction was not made for appendage to the pipette at these preliminary investigations. For each new liquid such a correction must be made by weighing the pipette when filled and after the drop has been blown out in order to ascertain the volume of liquid which remains in the pipette.

about two hours h was found to be in the interval $0.96 \text{ mm} \leq h \leq 100 \text{ mm}$. This value was found to be the same after 24 hours.

Therefore, measurements made in the air of an ordinary room must be made very quickly after cleaning of the glass sheet as the character of its surface evidently changes quickly, the surface probably being coated with a film of air, water vapour and dust. Since final value as well as initial value seem reproducible in this case, both are of interest.

Corresponding measurements were tried with a Carlsberg pipette of 80 mm^3 , and it was found that h of drops from this pipette, h_{80} were related to h_{40} in the ratio $\sqrt[3]{\frac{80}{40}}$, which shows that the drops of water have been uniform, and that gravity has not influenced the configuration even of drops having as large a volume as 80 mm^3 .

On the other hand the reproducibility seemed less good for drops of peanut oil and solutions of sulphonated products, and certain observations seemed to indicate phenomena of hysteresis. However, a systematic investigation according to the principles outlined might be of interest.

It has been shown above that measurements of such capillary-chemical quantities as interfacial tensions and contact angles can at any rate in principle be used for solution of the practical task of evaluating detergents.

Naturally this task could also be tackled from a different angle by simply carrying out dish washing on standard soiled plates in a fixed way, and research work on this principle is also done ⁵. But it would save time in practice if an evaluation could be made on the basis of quantities measurable in a quick and exact way.

SUMMARY

1. The reversible isothermal work in Dupré's equation is put forward as a measure of the efficiency of detergents.
2. The conditions for use and measurement of this quantity are discussed.
3. Antonoff's rule is shown to be invalid.
4. A new, simple method for measurement of contact angles is described.

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Received March 21, 1953.