The Definition and Affinity of the Deterging Process

PIERRE BARUËL

F.D.B.'s Centrallaboratorium, Copenhagen, Denmark

A system in which a deterging process takes place has so many variables that it is not a priori clear how to define the deterging process and its affinity. So the problem of how to evaluate detergents leads to a thermodynamical analysis of systems of the above kind with due regard to the practical purpose. Certain results of this analysis may be generalized for use in other evaluation problems. For the dish washing process, the writer has previously¹ suggested as affinity measure the adhesion work W_A in isothermal reversible separation of soil and detergency object when both phases are surrounded by the detergent analogous with Dupré's definition concerning the separation of two phases surrounded by air. The significance and reasons are explained quantitatively for applying this, the simplest possible, thermodynamically justifiable, convention. The expression for W_A comprises interfacial tensions between solid-liquid phases, but may be rewritten in various ways to make it accessible to experimental determination.

1. EVALUATION OF DETERGENTS

The evaluation of a detergent is most often done in one of the following ways:

- A. by practical washing tests, or
- B. by measuring its surface tension γ_{DG} against air at varying concentrations.

The latter method was, at any rate, in common use during the early stages of synthetic detergents. The former method takes long time and presents certain practical difficulties. The latter method — according to which the detergent showing lowest surface tension at lowest concentration is claimed to be best — is based on the determination of quantities easily accessible to accurate measurement; but the method is lacking a well-grounded experimental and theoretical foundation.

Now the question arises whether it is possible either to establish method B or to substitute for it another, more well-founded method with similar favourable properties.

Fig. 1.

A pre-condition for solving this problem — or altogether to attach any meaning to it — is above all the *postulate* that method A can lead to an unambiguous evaluation of the efficacy of various detergents (referred to in the following as D-agents), *i. e.* that in practice the variations in the washing method are insignificant so as not to influence the evaluation. To this postulate the writer has¹, as far as dish washing agents are concerned, added that the quantity:

$$W_A = -\gamma_{PO} + \gamma_{PD} + \gamma_{OD} \quad (1)$$

shows accordance with this evaluation and that γ_{DG} does not, if:

γ_{XY} = interfacial tension between X and Y

P = the detergency object (porcelain)

O = the soil (oil)

D = D-agent

G = air

The thermodynamical significance of the quantity W_A will appear from the following. Now the question is whether the above statement can be established.

2. CONVENTIONS AND FACTS

As a model to which the considerations may be appropriately attached, we will consider a system as shown in Fig. 1.

It consists of a detergent system composed of a vessel with a P-plate, an O-drop and a large D-phase. The detergent system is surrounded by the atmosphere G. Furthermore, there is a reservoir for mechanical energy R (R represents the washing machine or the person that does the dish washing).

In order to evaluate D as a dish washing agent, it is necessary to define what to understand by a deterging process in the detergent system by fixing its initial and final state. However, this is not quite so simple as it may seem to be. What is usually called a dish washing consists of a series of more or less well-defined operations during which a detergent system passes through a succession of state changes $a_1 \rightarrow a_2 \rightarrow a_3 \dots$. Examples of such links $a_i \rightarrow a_{i+1}$ are: the detergent's solution in water, the placing of P (with O) in the D-phase, overcoming the adhesion O—P. If the link $a_i \rightarrow a_{i+1}$ is spontaneous, it would mean that $a_i \rightarrow a_{i+1}$ occurs in the detergent system even if R is not coupled in. In these circumstances the process naturally entails an entropy increase ΔS

in the detergent system plus surrounding G-phase, with which the detergent system is in thermal contact. By introducing R, an amount of energy $\Delta E_R = T\Delta S$ could be gained if the process $a_i \rightarrow a_{i+1}$ takes place at maximum utilization, T being the temperature (in $^{\circ}\text{K}$).

If we consider two detergents during the course of $a_i \rightarrow a_{i+1}$ in two detergent systems, one would be apt to suppose that the detergent with the highest value of ΔE_R had functioned best during the operation $a_i \rightarrow a_{i+1}$ because it is useful energy (in R) we want to save. There is, however, the *essential qualification* to add in this *practical* example that it must be possible to couple R to the detergent system. If *e. g.* we consider the operation of the pure detergent's solution in water, we have clearly a spontaneous link which theoretically might be utilized. It is, however, quite irrelevant to the practical evaluation of the two detergents whether one detergent might *theoretically* give greater gain of energy in R than the other at the above dissolution, since there is no possibility of coupling. If only the link is spontaneous, we are satisfied. What is desired is to save useful energy in those links which in practice correspond to coupling. In order to obtain comparable values for these links, it is necessary to use maximum utilization (reversible coupling), because the possibilities of utilization are not known in detail. Broadly it can be said that it is of no use *e. g.* to be able theoretically to gain much mixing work by the detergent's solution in water, if later on O adheres very strongly to P. *Thus there exist a number of links which must not be included in the definition of the deterging process for our purpose*, since the only requirement is that they are spontaneous. It might be expedient to include this requirement in the definition of a detergent. As such links the writer has also grouped the wetting and de-wetting processes in the immersion and removal of P into and from the D-phase. *But possibly this assumption is too rough as it would certainly be for textiles.*

In accordance with what is said above, it is now the task to try to define the initial state a and the final state b for the deterging process in the system illustrated in Fig. 1. It will soon appear that the fixing of a and b involves uncertainties owing to lack of knowledge of the kinetics of practical dish washing. The only approach is, therefore, — at any rate for the time being — to remove the uncertainties through conventions. After selecting conventions for the fixing of a and b , the efficacy measure for D will be the reversible isothermal work W that might be gained by the introduction of R if the process $a \rightarrow b$ takes place in the detergent system.* The experimental proof that the states a and b are properly chosen must be obtained from a large-scale examination of the connection between this value and evaluations by the above method A. The theoretical establishment lies in the fact that W denotes ΔE_R for a (idealized, it is true) deterging process, whereas γ_{DG} measured alone (method B) does not refer to anything at all with relation to what causes trouble and expenses in a deterging process. As conventions we would of course in the first instance select the simplest that are not incompatible with what is said above.

Let us consider first the final state b . In this state O must be removed from P, and be surrounded by D (or perhaps D and G). In traditional thermodynamics states of equilibrium are widely operated with, but for our purpose

* *i. e.* the work done by R with inverted sign.

it must be noted that after overcoming the adhesion O—P, O may assume any shape as shown in Fig. 2 where only the sphere at extreme right could represent mechanical equilibrium.

Fig. 2.

Broadly it can be said that the removal of O in unchanged shape (extreme left, Fig. 2) corresponds to an instantaneous "cutting off", and the sphere to a slow "rolling off" of O. The higher O's viscosity is, the easier it is to imagine the removal in unchanged shape. If b is defined as corresponding to the latter, and imagined realized, it would if the detergent system is left to itself be followed by a process $b \rightarrow b_0$ (Fig. 3), which might have done useful work.

Fig. 3.

This theoretically obtainable work would be of no use in practice if practice corresponds to a "cutting off". If so, D should have "assisted in" the "cutting off". In practice it would most likely be somewhere between the said possibilities. Quite similar uncertainties are encountered when trying to fix the initial state a .

If a represents the state when O's removal is started, it would be possible to include in the definition certain preceding links $a_0 \rightarrow a$ (Fig. 3). When comparing two detergents one must consider the same O-amount adhering to P before immersion into the D-phases, and if a represents the state immediately after the immersion, O has at state a the same area σ_{PO} in common with P as in the air before the immersion. If the detergent system is left to itself before the removal, the area σ_{PO} will change through a spontaneous process, partly because of an interchange of matter between O and D during mutual dissolution, and partly because γ_{OG} and γ_{PG} are replaced by γ_{OD} and γ_{PD} . Also here we are lacking in kinetic knowledge. Are *e. g.* the processes of interchange of matter allowed time to occur in practice and "to lend a hand", or do they not attain any importance until state b_0 (Fig. 3) is reached?

This important point will be touched later; here we shall only point out that processes of the type $a_0 \rightarrow a$ do not necessarily always "lend a hand". If the detergent is pure water, more water will be dissolved *e. g.* in oleic acid than the other way round. O's volume is not always reduced and the equilibrium tensions may have spread O over P. Perhaps it would not be quite reasonable to consider pure water a detergent for dish washing. If we assume, however, that processes of the kind $a_0 \rightarrow a$ and $b \rightarrow b_0$ "lend a hand", we would (by leaving them out of the definition of the deterging process) *never obtain too optimistic an evaluation* of the detergent through ΔE_R for the process $a \rightarrow b$. This means some safety in an evaluation where it is impossible to state with certainty what is the "right" set of conventions. To the above considerations may be added that some of them are of quite a general nature and apply to all evaluations where it is a question of carrying through certain processes by means of certain agents *.

3. QUANTITATIVE THERMODYNAMICAL TREATMENT

a. the Energy differential

We can now make a stringent summary of the foregoing and at the same time study the properties of W_A through a quantitative thermodynamical treatment.

if:

E	represents	energy
S	»	entropy
v	»	volume
σ	»	interfacial area
n_i	»	number of moles of substance i
T	»	temperature
p	»	pressure
μ_i^f	»	chemical potential for substance i in phase f
γ	»	interfacial tension
Index K	»	interfacial layers (referred to in the following as capillary phases)
Σ_i	»	summation over the substances
Σ_f	»	» » » phases

we have for states in the detergent system with homogeneous bulk phases:

$$dE = \sum_f T dS - \sum_f p dv + \sum_f \sum_i \mu_i^f dn_i^f + \sum_K \gamma d\sigma$$

from which is obtained the maximum isothermal work dE_R which by a differential process can be gained in R by leaving out $\sum_f T dS$ and $p dv'$ as $-dv' = dv_0 + dv_D$ is introduced and the sign inverted.

* Examples of quite another kind of evaluations are *e. g.* organoleptic tests.

Thus we find:

$$dE_R = (p_0 - p_D)dv_0 - \gamma_{PO}d\sigma_{PO} - \gamma_{PD}d\sigma_{PD} - \gamma_{OD}d\sigma_{OD} - \sum_i \mu_i^f dn_i^f \quad (2)$$

We now find that on certain assumptions (2) is converted to:

$$dE_R = (\gamma_{PO} - \gamma_{PD} - \gamma_{OD})d\sigma_{PD} = -W_A d\sigma_{PD} \quad (3)$$

Above all, we have simplified the problem by leaving out of consideration gravity, buoyancy and electric charges in the phases, since (2) does not contain variables representing these phenomena. Furthermore, we have put $dv_0 = 0$ and $-d\sigma_{PO} = d\sigma_{PD} = d\sigma_{OD}$ which corresponds to a removal of the drop in unchanged shape. Finally we have put:

$$\sum \mu_i dn_i = 0 \quad (4)$$

which causes the greatest difficulties.

b. W_A^{initial} and W_A^{final}

A safe way of fulfilling (4) is to operate with material equilibrium in the detergent system during the process. In that case no chemical processes will occur (hydrolysis etc.) and the phases are mutually saturated throughout the process.

The detergent system has, besides the degrees of freedom of a simple thermodynamic system (pressure (p) — temperature (T) — and concentrations (c) in all phases) as many — f_k — further degrees of freedom as there are capillary phases, but accordingly also f_k further phases which are to be taken into consideration with their concentrations. If f_0 represents the number of bulk phases, x the number of degrees of freedom, and κ the number of components, the phase rule will accordingly maintain its form:

$$f_0 + x = \kappa + 2 \quad (5)$$

Actually, this is not quite correct, because the bulk phases are usually of different pressure owing to curved capillary phases, but as we are considering condensed systems, we can with approximation disregard the effect of the pressure on the potentials provided the curvature of the interfaces is not very pronounced (as in very small drops). As furthermore the external pressure and the temperature are fixed in our system, the phase rule is expressed by:

$$f_0 + x = \kappa \quad (5 \text{ a})$$

Here x is the same whether or not we group porcelain under f_0 and κ . Irrespective of the "additional" degrees of freedom it can accordingly be laid down that in a 2-component-system (e.g. oil-water) (or in a 3-component-system, if we include the P-phase) $x = 0$, that is to say we have a fixed composition of the

* Here we treat the K-phases as mathematical surfaces without volumes according to Gibbs. Alternatively, they may be considered of arbitrary volumes. The result is with good approximation the same. Regarding this problem reference is made e.g. to Guggenheim's *Thermodynamics* ².

phases and fixed interfacial tensions throughout the process. In a 3-component-system (*e. g.* oil-water-synthetic detergent) (or in a 4-component-system, when including P) $x = 1$, *i. e.* the same as above holds if we fix D's concentration C_D .

By the above considerations we have, however, accounted only for the intensive states of the phases when $a \rightarrow b$ is imagined taking place at material equilibrium, but the detergent system, being materially isolated, is subject also to constraints of extensive nature, namely stoichiometric relations, since the amounts of the capillary phases vary.

However, we assume that the D-phase is large in relation to O, and accordingly that $C_D = \text{constant} = \text{initial value}$ during the process $a \rightarrow b$. According to common thermodynamical parlance this simplifying assumption can be so expressed that the dish-washing process under consideration is regarded as a differential process. Accordingly, (3) can be immediately integrated assuming constant tensions. We will designate W_A by the above described process (at material equilibrium) W_A^{final} and accordingly we obtain (Δ representing finite differences and γ^{final} the γ 's corresponding to the process):

$$\frac{dE_R}{d\sigma_{PD}} = \frac{\Delta E_R}{\Delta\sigma_{PD}} = -W_A^{\text{final}} = \gamma_{PO}^{\text{final}} - \gamma_{PD}^{\text{final}} - \gamma_{OD}^{\text{final}}$$

There is, however, quite another way of satisfying (4): The material changes may be insignificant, *i. e.* it may with approximation be possible to put $dn_i^f = 0$. This cannot be attained completely throughout the process, because the variations in the interfacial areas entail transferring of matter between bulk phases and capillary phases. If we disregard this, it is possible in certain cases to leave out of consideration irreversible transferring of matter caused by material disequilibrium. Such transferring may be so slow, or the duration of the process so short, as to make it insignificant. They may also be imagined blocked. If we regard the detergent system at a state immediately after new D—O and P-surfaces having been brought in contact, the tensions in the interfaces would have certain more or less well-defined values γ^{initial} . Such tensions are in literature often called "dynamical tensions". The quantity W_A (1) computed with these tension values, we will call W_A^{initial} . This quantity corresponds to $\Delta E_R = \int dE_R$ by a reversible removal with blocked material processes, provided we disregard the work $\sum \sum \mu dn$ corresponding to the area-work in connection with transferring of matter owing to chemical potential differences between bulk- and capillary phases. This assumption will not be dealt with in this paper. We would only point out that the introduction of W_A^{initial} and W_A^{final} corresponds to the — in literature³ well-known — definition of initial and final values of the so-called spreading coefficients, and that we can, of course, in the same manner as introducing a semi-initial value for these, imagine $W_A^{\text{semiinitial}}$ or $W_A^{\text{semifinal}}$ defined. W_A^{final} or $W_A^{\text{semifinal}}$ corresponds in practice to the final states of a dish washing comprising a large number of washing objects in the vessel where the D-phase has not been renewed.

c. Properties of W_A .

Now it is also easily seen that the quantity W_A has a relation to spreading phenomena. This fact is immediately realised if we let O and D (Fig. 1) exchange roles. We imagine in other words a D-drop adhering to P and a large surrounding O-phase. Further, we imagine the D-drop widely spread — possibly through external influence — so that the contact angle is practically $= 0$. The concentration of the drop must be $= C_D$ in the removal test from which is obtained W_A for an O-drop on P surrounded by D. For further spreading of the D-drop we approximately have:

$$d\sigma = d\sigma_{PD} = -d\sigma_{PO} = d\sigma_{DO} \text{ and } p_D = p_O$$

and hence (2) for $\Sigma \Sigma \mu dn = 0$ making

$$\begin{aligned} dE_R &= (\gamma_{PO} - \gamma_{PD} - \gamma_{DO}) d\sigma = P d\sigma \\ \text{or} \quad dE_R &= -W_A d\sigma \end{aligned}$$

where $d\sigma > 0$ for spreading, and W_A refers to the originally considered process, *i. e.* removal of the O-drop. Indicating the drop with index and as above the spreading coefficient with P, we have with easily understood designations:

$$\begin{aligned} P^D &= -W_A^O \text{ and specially also} \\ P^{D, \text{final}} &= -W_A^{O, \text{final}} \end{aligned} \quad (6)$$

However P^{final} must be < 0 (*cf.*³)

Thus it follows from (6) that we always will have:

$$W_A^{O, \text{final}} > 0 \quad (6 \text{ a})$$

while nothing prevents

$$W_A^{O, \text{initial}} \text{ from being } \geq 0$$

Now it will be natural to examine the significance of W_A 's sign. Let us assume that the detergent system is in stable equilibrium with an O-drop adhering to P and with contact angle Θ . It is now easily derived that

$$W_A^{\text{final}} = \gamma_{OD}^{\text{final}} (1 + \cos \Theta)^{\text{final}} \quad (7)$$

whence — leaving out index 'final' — follows:

$$0 \leq W_A \leq 2\gamma_{OD} \quad (7 \text{ a})$$

which is accordingly a condition for stable drop on P. It is, however, clearly seen that this condition is not sufficient, for an evaluation of stability concerns ΔE_R by the process $a \rightarrow b_0$ (Fig. 3) where b_0 is the state of equilibrium upon removal and not ΔE_R by the process $a \rightarrow b$. We have now with easily understood symbols:

$$\Delta E_R (a \rightarrow b_0) = \Delta E_R (a \rightarrow b) + \Delta E_R (b \rightarrow b_0)$$

or per unit area of the surface PO according to (2)

$$\Delta E_R (a \rightarrow b_0) = -W_A - \gamma_{OD} \Delta \sigma_{OD} (b \rightarrow b_0) + (p_O - p_D) \Delta v_0 (b \rightarrow b_0) \quad (8)$$

or when expressing the latter part by W' :

$$\Delta E_R (a \rightarrow b_0) = -W_A + W' \quad (8 \text{ a})$$

where, owing to $b \rightarrow b_0$'s spontaneousness $W' > 0$

if $-W_A + W' > 0$, the drop is not stable;
if $-W_A + W' < 0$, the drop is stable.

Here it must, however, be remembered that gravity, buoyancy and electric charges are left out of consideration. It is, of course, possible to compute W' on certain simple assumptions. If once again we presuppose that the change in pressure by variation in curvature through the change spherical cap $\rightarrow$ sphere, is of no consequence to the solubility equilibrium, so that the above process takes place without movement of matter between the phases, and if further — more we disregard the change in volume through the increase in pressure — which is, of course, a good approximation — we have in (8): $\Delta v_0 = 0$, and $W' = -\gamma_{OD} \Delta \sigma$.

By simple, but somewhat lengthy geometrical computations¹ we find on these assumptions:

$$W' = \gamma_{OD} (2 + t^2 - (t^3 + 3t)^{\frac{2}{3}})$$

where t = tangent of the spherical cap's half contact angle.

As corresponding values can e. g. be given:

$$\begin{aligned} t = 0, & \quad W' = 2\gamma_{OD} \\ t = \frac{1}{2}, & \quad W' = 0.87\gamma_{OD} \\ t = 1, & \quad W' = 0.5\gamma_{OD} \\ t = 2, & \quad W' = 0.2\gamma_{OD} \end{aligned}$$

The term W' in (8 a) accounts for processes of the kind $b \rightarrow b_0$ (Fig. 3). But as pointed out above, it is by no means certain that these links or the links $a_0 \rightarrow a$ should be taken into consideration when fixing a practical evaluation measure for D-agents. As regards processes of the kind $a_0 \rightarrow a$, they will not be discussed in detail in this paper. We would only point out that on certain assumptions we learn something also about such processes from the quantities W_A and γ_{OD} . Let us assume that we have a stable O-drop on the P-plate for two D-agents I and II. From (7) is obtained, leaving out indices "final":

$$\cos \Theta_I - \cos \Theta_{II} = \frac{W_A^I}{\gamma_{OD}^I} - \frac{W_A^{II}}{\gamma_{OD}^{II}}$$

which determines whether

$$\Theta_I \begin{matrix} \geq \\ \leq \end{matrix} \Theta_{II}$$

If, therefore, the dissolving processes do not change the conditions, it will be known which final area is the larger when the drops were equal at the outset.

4. EXPERIMENTAL INVESTIGATIONS AND SOME KINETIC CONSIDERATIONS

Designating with θ_{xy}^z the contact angle between phases X and Y when X and Y are surrounded by phase Z, the equation (7) will be:

$$W_A = \gamma_{OD} (1 + \cos \theta_{PO}^D) \quad (7)$$

This equation can be used for the determination of W_A through measuring γ_{OD} and θ_{PO}^D ; always provided, of course, that the drop is stable. Thus it will *e. g.* not be applicable to the determination of negative W_A -values (*cf.* 7 a). In a previous paper¹ the writer suggested for various reasons the application of another equation, namely:

$$W_A = \gamma_{OG} \cos \theta_{PO}^G - \gamma_{DG} \cos \theta_{PD}^G + \gamma_{OD} \quad (9)$$

According to (9) the contact angles for O- and D-drops are measured against air (G). Its validity is, however — as can be shown by a detailed analysis — subject to a number of pre-conditions which in practice can only with difficulty be fulfilled; and if they are not fulfilled, the results arrived at would be quite wrong. Consequently the writer now considers this equation of merely theoretical interest. A series of experiments have been carried out with D-agents, peanut oil and glass in accordance with (9), which were described in the original manuscript, but as the writer has changed his technique*, he thinks it more reasonable to mention some comments received from several researchers during the exchange of experiences. This exchange has also directed the writer's attention to various available works in the detergent literature. Of interest are *e.g.* works by Kling^{4,5}.

Strange enough, there have been no objections to the practical application of (9), but the chief objection seems to be that the velocity has been ignored in the considerations advanced in¹. The velocity is by some researchers considered of even primary importance. To this objection should above all be said that the velocity for the washing process cannot be unambiguously connected with the detergent system as such, for a dish-washing is not done by placing the washing objects in a vessel with the D-agent and then just sit back and wait, *i.e.* to leave the system alone. The velocity is a factor that is influenced by the operator, provided it is not — for certain processes $a_i \rightarrow a_{i+1}$ — so extremely high that they occur before the operator interferes.

Another objection is that the drop can practically always come loose by itself — quickly or slowly — so that there will be no contact angle. ($\cos \theta_{PO}^D$ in (7) is undefined).

So the drop is said to be unstable and consequently it is possible for the system to do the washing by itself releasing free energy. If this is so for two D-agents, no energy will *in principle* be required to hasten the attainment of the final state if it is possible reversibly to recover the kinetic energy. *The two D-agents might then be considered equally good* quite irrespective of which of them releases most free energy when left to themselves. Now such reversible

* With the kind assistance of the Danish technical University, dpt. of technical physics, a very simple device has been designed for measurements in accordance with (7).

recovery will not be possible in practice. If we, however, consider two systems I and II in which the spontaneous dish-washing takes place, quickly and slowly respectively, the question arises: What causes the retardation of one drop in relation to the other?

The velocities are determined by 1) the pressure gradients 2) the weight of the drops 3) the friction (viscosity) 4) the charges in the interfaces (and the phases) 5) the adhesion as expressed *e. g.* in W_A and γ_{OD} (disregarding any dissolving processes).

1) and 2) must be about equal for I and II — (the specific gravity is about 1 for both D-solutions and we are considering the same O-amount and O-kind).

As the systems are liquid, we can with approximation disregard 3) as the cause of retardation in II, for the friction is very small when the process is slow. Then 4) and 5) remain. We have in these preliminary considerations ignored 4). Thus W_A will be highly co-responsible for the velocity of the spontaneous washing process. Roughly, it can be said, u representing the velocity and f a function

$$u_I - u_{II} = f(W_A^I, \gamma_{OD}^I, \Delta E_R^I, W_A^{II}, \gamma_{OD}^{II}, \Delta E_R^{II})$$

assuming that we now influence the systems from outside. (The consideration is of course very *rough*, particularly because it is not a question of a single value of velocity but of a velocity field. The writer is striving to establish the considerations in a quantitative form). Accordingly, if we want to bring about the same velocity (velocity field) in I and II, and if we know the W_A 's and the γ_{OD} 's, the difference between the two required values of ΔE_R is determined by that knowledge.

Finally should be said: It will often be found that the drop is removed *almost* by itself when the P-plate is placed so that the buoyancy assists in removing it. According to the writers' experiences this is strongly dependent on the pre-treatment of the plate. As pure water gives a defined contact angle D's concentration must also be taken into consideration.

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Received January 22, 1954.