

A QUANTITATIVE KINETIC THEORY OF EMULSION TYPE. I. PHYSICAL CHEMISTRY OF THE EMULSIFYING AGENT

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Emulsion type is often related to the preferential solubility of the emulsifying agent in one of the Phases (Bancroft rule). Recently, however, emulsion type has been interpreted quantitatively, though purely empirically, according to the hydrophilic-lipophilic balance (HLB) classification. The relation of HLB numbers to the solubility of the emulsifying agent in the oil or water phases is discussed, and both the Bancroft rule and the HLB system are compared with a quantitative kinetic theory of emulsion type.

If a mixture of oil and water is agitated in the presence of a surface active agent as emulsifier, an emulsion will result. Will this emulsion be oil-in-water (O/W) or water-in-oil (W/O) ? This question has long been of interest: apart from the particular surface active agent chosen, such factors as the method of dispersion¹⁻⁶, the phase volume⁵⁻⁸ and the viscosities of the phases^{5,6} may greatly influence the type of the resultant emulsion.

Among the various theories of emulsion type suggested during the last half-century may be mentioned the *Bancroft rule*^{9,10}: this states that the phase in which the stabilizing agent is more soluble will be the continuous phase. This was put forward as a purely empirical correlation, but Cassel's thermodynamic reasoning^{11,12} was believed to have placed the Bancroft rule on a firm basis^{5,10}; Cassel's treatment, however, is open to serious criticism and will not be considered further.

That different stabilizers led to *preferential curvature of the oil/water interface* was first suggested under the title of the 'oriented wedge' theory⁵. The latter is now of historical interest only, but the idea that preferential interfacial curvature will determine emulsion type has recently been revived by Cassel^{11,12} (who used it in an attempt to justify the Bancroft rule), and by Griffin¹³. That the radii of curvature of emulsion drops are of the order one thousand times molecular dimensions would seem, however, to minimize the practical effect of any molecular tendency to preferential curvature.

Recently, emulsifying agents have been classified numerically on the '*HLB*' scale¹³⁻¹⁶; this refers to the hydrophilic-lipophilic balance of the emulsifier molecule, and is related to oil and water solubilities. The correlation of HLB and emulsion type is based on direct experimental tests, though for some systems the HLB value can be estimated by empirical rules from the analysis of the surface active agent^{15,16}.

In the present paper, the *coalescence kinetics* are considered responsible for emulsion type. The kinetics of emulsion breaking^{2,5} have long been of interest, and Cheesman and King² and

McBain¹⁰ pointed out the importance of such kinetics in determining emulsion type. The same idea was also suggested in connection with simple 'model' experiments¹⁷⁻¹⁹ on the relative coalescence rates of oil drops with an adjacent oil phase and of water drops with an adjacent aqueous phase. This idea is extended in the present paper, using recent findings on the mechanism of coalescence²⁰⁻²³. Briefly, the two systems in Figures 1 and 2 are compared; the corresponding emulsion will be W/O if the rate of coalescence in Figure 1 is greater than that

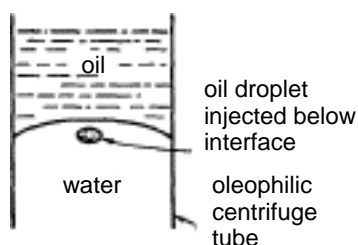


Figure 1: Model system for studying coalescence rates for O/W systems

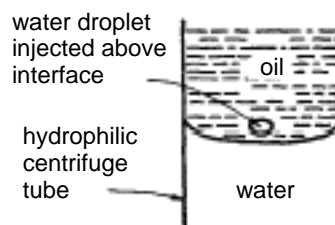


Figure 2: Model system for studying coalescence rates for W/O systems

in Figure 2; if the rate of the second process is greater than the first, the emulsion will be O/W. Mechanical and hydrodynamic effect will be considered separately in a future publication.

The quantitative theory of emulsion type as here developed leads to nine quantitative relations, embodying the following conclusions:

- (i) emulsion type depends only on the relative rates of coalescence of oil-in-water and water-in-oil systems;
- (ii) the logarithm of the relative coalescence rates should vary directly with the HLB values for different emulsifiers;
- (iii) while the Bancroft rule cannot have a *thermodynamic* basis, a strict correlation has been found theoretically between the relative *coalescence rates* (Figures 1 and 2) and the preferential solubility of different emulsifiers in one of the phases, under certain conditions;
- (iv) the empirical HLB values have a fundamental significance in terms of free energies, and should be related to the distribution of surface active agent between oil and water under certain conditions.

Coalescence rates

Consider two oil phases separated by water (Figure 1) and two water phases separated by oil (Figure 2), parts of the system formed from oil and water during agitation (Figures 3 and 4).

Suppose now that the oil surfaces in Figure 1 are electrically charged: they repel each other as they approach, and the chance that the surfaces will come within the required few ångström units for oil to bridge the gap between them will be lower than if they had been neutral. The coalescence rate, Rate_1 , of the O/W emulsion corresponding to the system in Figure 1, will thus be a function not only of a hydrodynamic collision factor A_1 (including the phase volume of oil and the viscosity of water), but also of the energy barrier due to the electrical potential ϕ_0 of the surfaces

$$\text{Rate}_1 = A_1 \exp\left(-0.24 \frac{\phi_0^2}{R T}\right) \quad \dots (1)$$

In this equation, derived in Appendix I, R is the gas constant in cal mole⁻¹ units and ϕ_0 is expressed in millivolts. The term ϕ_0^2 in the exponential bracket explains the extreme sensitivity of emulsions to a small increase in the salt concentration^{5,24}: this will slightly reduce ϕ_0 (see Appendix I), and hence, according to equation (1), Rate₁ is greatly increased.

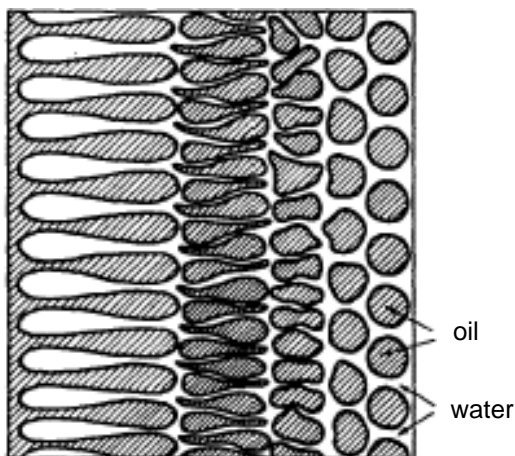


Figure 3

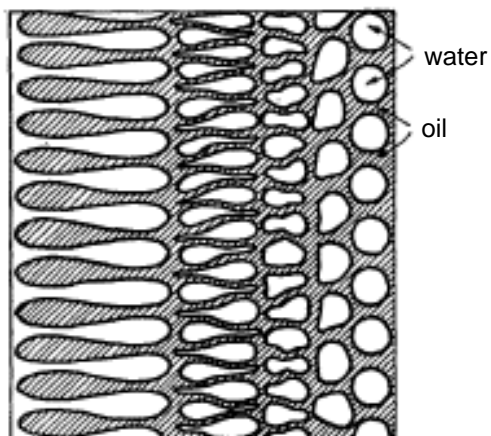


Figure 4

Figures 3 and 4. Emulsification procedure (left-hand side of figures) may lead to both O/W and W/O systems simultaneously: which type is finally observed will depend on the relative coalescence rates of the two systems. If the system in Figure 3 is stable, whereas that in Figure 4 breaks very rapidly, the emulsion type will be O/W, and vice versa.

Some stabilizing agents are uncharged, and act by binding water tightly to the surface of the drops. This water of hydration must be displaced before the two oil drops in Figure 1 can coalesce: the total energy barrier E_h required for this displacement will depend on the number and type of the hydrated groups on each molecule of the surface-active agent and on θ , the fraction of the interface covered

$$\text{Rate}_1 = A_1 \exp\left(-\frac{E_h}{R T}\right) \quad \dots(2)$$

If the emulsifier contains only a single -OH group, this will hold a molecule of water by a weak hydrogen bond of energy about 4000 calories. For the two oil surfaces nearly in contact, as in Figure 1, the binding energy will amount to 8000 calories, but this will be

decreased finally to perhaps 4000 calories because on coalescence the two displaced water molecules will now hydrogen-bond with each other. Thus, for this system if $f = 1$,

$$\text{Rate}_1 = A_1 \exp(-4000/RT)$$

In general, both charge and hydration may be operative in decreasing Rate_1 , and the two energy barriers act simultaneously

$$\text{Rate}_1 = A_1 \exp\left\{\left(-0.24 \frac{z^2}{r_0} - E_h\right)/RT\right\} \quad \dots (3)$$

This can explain quantitatively the findings of Schulman and Cockbain²⁵ that the addition of a long-chain alcohol to a detergent-stabilized O/W emulsion may greatly enhance its stability, even though the alcohol alone would favour a W/O emulsion: both electrical and hydration factors are now operative.

The inverse system of two water surfaces separated by non-polar oil (Figure 2) will coalesce by the water bridging the oil gap when the drops approach as close as possible. The rate of coalescence will thus depend both on hydrodynamic factors (included in the term A_2), on the number n of $-\text{CH}_2-$ groups in each hydrocarbon chain and on θ , the fraction of surface actually covered with surface active emulsifier²⁶⁻²⁸. The barrier of each $-\text{CH}_2-$ group to the passage of water²⁹ is about 300 cal and, since in the system of Figure 2 the water will have to bridge the gap across $2n$ $-\text{CH}_2-$ groups

$$\text{Rate}_2 = A_2 \exp(-2n \times 300/RT) \quad \dots(4)$$

Combination of equations (3) and (4) leads to

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{A_2}{A_1} \exp\left\{\frac{+0.24 \frac{z^2}{r_0} + E_h - 600n}{RT}\right\} \quad \dots(5)$$

and we have by definition the further relation

$$t_1/t_2 = \text{Rate}_2/\text{Rate}_1 \quad \dots(6)$$

where t_1 and t_2 are the times required for coalescence in the systems of Figures 1 and 2.

If now, on agitating a mixture of oil and water with an emulsifying agent, we form either a mixture of systems of the types of Figures 1 and 2, or systems as in Figures 3 and 4, we shall suppose that the relative coalescence rates will determine the emulsion type as observed shortly after the agitation is stopped¹⁷⁻¹⁹. Hence we have the relations

$$\text{O/W emulsion formed if } t_1/t_2 \gg 1 \text{ or } \text{Rate}_2/\text{Rate}_1 \gg 1 \quad \dots(7)$$

$$\text{W/O emulsion formed if } t_1/t_2 \ll 1 \text{ or } \text{Rate}_2/\text{Rate}_1 \ll 1 \quad \dots(8)$$

These inequalities referring to *emulsion type* have been verified experimentally^{17,18}. In the present paper they will be related to the HLB classification and the Bancroft rule. The emulsion will be *stable* (e.g. for a year) only if Rate_1 or Rate_2 is smaller than 10^{-6} A.

The hydrophilic-lipophilic balance (HLB) of the emulsifier

The HLB values^{13-16,30} represent an empirical numerical correlation of the emulsifying and solubilizing properties of different surface active agents.

Table I illustrates the various ranges of HLB values, and the actual values found experimentally for some different surface active agents are shown in Table II.

Table I. Classification of emulsifiers according to HLB Values^{15,30}

| <i>Range of HLB values</i> | <i>Application</i> |
|----------------------------|-----------------------|
| 3.5-6 | <i>W/O emulsifier</i> |
| 7-9 | <i>Wetting agent</i> |
| 8-18 | <i>O/W emulsifier</i> |
| 13-15 | <i>Detergent</i> |
| 15-18 | <i>Solubilization</i> |

Table II

| Surface active agent | HLB from expt. ^{13,15,16,30-32} | HLB from group numbers of table III |
|---|--|-------------------------------------|
| Na Lauryl sulphate | 40 | (40) |
| K Oleate | 20 | (20) |
| Na Oleate | 18 | (18) |
| Tween 80 (sorbitan "mono-oleate" + 20(CH ₂ -CH ₂ -O) groups) | 15 | 15.8 |
| Sorbitan "mono-oleate" + 10(CH ₂ -CH ₂ -O) groups | <i>about 13.5</i> | 12.5 |
| Tween 81 (sorbitan "mono-oleate" + 5(CH ₂ -CH ₂ -O) groups) | 10 | 10.9 |
| C ₁₈ H ₃₇ N(CH ₂ CH ₂ OH)(CH ₂ -CH ₂ -O-CH ₂ CH ₂ OH) | 10 | (10) |
| Sorbitan monolaurate | 8.6 | 8.5 |
| Methanol | - | 8.4 |
| Ethanol | - | 7.9 |
| n-Propanol | - | 7.4 |
| Sorbitan "mono-oleate" + 2(CH ₂ -CH ₂ -O) groups | <i>about 7</i> | 7.0 |
| n-Butanol | 7.0 | 7.0 |
| Sorbitol "mono-oleate" | <i>about 7</i> | 7.2 |
| Sorbitan monopalmitate | 6.7 | 6.6 |
| Sorbitan monostearate | 5.9 | 5.7 |
| Span 80 (sorbitan "mono-oleate") | 4.3 ? | 5.0 |
| Propylene-glycol monolaurate | 4.5 | 4.6 |
| Sorbitan distearate | <i>about 3.5</i> | 3.9 |
| Glycerol monostearate | 3.8 | 3.7 |
| Propylene-glycol monostearate | 3.4 ? | 1.8 |
| | <i>(may contain soap)</i> | |
| Sorbitan tristearate | 2.1 | 2.1 |
| Cetyl alcohol | 1 | 1.3 |
| Oleic acid | 1 | (1) |
| Sorbitan tetrastearate | <i>about 0.5</i> | 0.3 |

Calculated values for 'mono-oleates' assume these are 1.38 oleates³²

The present author has found that HLB values for surface active agents can be consistently calculated directly from the chemical formulae, using *group numbers*. Table III shows these group numbers, from which the HLB values in the last column of Table II have been calculated, using the relation

$$\text{HLB} = \Sigma (\text{hydrophilic group numbers}) - n (\text{group number per CH}_2 \text{ group}) + 7 \dots (9)$$

Here *n* is again the number of -CH₂- groups in the molecule of emulsifying agent. It must be emphasized that the HLB system is not concerned with the stability of the emulsion once formed: it is only a correlation of function (Table I), not of efficacy^{15,30}.

Table III. HLB Group Number

| <i>Hydrophilic groups</i> | <i>Group Number</i> |
|--|---------------------|
| -SO ₄ Na ⁺ | 38.7 |
| -COO ⁻ K ⁺ | 21.1 |
| -COO ⁻ Na ⁺ | 19.1 |
| N (tertiary amine) | 9.4 |
| Ester (sorbitan ring) | 6.8 |
| Ester (free) | 2.4 |
| -COOH | 2.1 |
| Hydroxyl (free) | 1.9 |
| -O- | 1.3 |
| Hydroxyl (sorbitan ring) | 0.5 |
| <i>Lipophilic groups</i> | |
| -CH- | - 0.475 |
| -CH ₂ - | |
| CH ₃ - | |
| =CH- | |
| <i>Derived groups</i> | |
| -(CH ₂ -CH ₂ -O)- | + 0.33 |
| -(CH ₂ -CH ₂ -CH ₂ -O)- | - 0.15 |

HLB group numbers to be used in equation (9). Results for different surface active agents are summarized in Table II. Note that the ethylene-oxide residue is hydrophilic, while the propylene-oxide residue is calculated to be lipophilic. These values for the residues will not hold for very large molecules, when for example there are 200 ethylene-oxide residues, since then different parts of the same molecule act virtually independently: in practice there is an upper limit to the HLB value of about 20 for high molecular polyethylene-oxide derivatives^{15,16,32}.

Relation of HLB values to coalescence rates

In logarithmic form equation (5) is

$$RT \ln \frac{\text{Rate}_2}{\text{Rate}_1} = RT \ln \frac{A_2}{A_1} + \left(0.24 \frac{2}{0} + E_h - 600n \right) \dots(10)$$

and, if the viscosities and phase-volumes of oil and water are equal (e.g. we have equal amounts of decane and water), A₂ = A₁ and so this relation involves only fundamental quantities

$$RT \ln \frac{\text{Rate}_2}{\text{Rate}_1} = 0.24 \frac{2}{0} + E_h - 600n \dots(11)$$

This may be compared with equation (9) into which the figure of 0.475 from Table III has been substituted

$$(\text{HLB} - 7) = (\text{hydrophilic group numbers}) - n \times 0.475 \dots (12)$$

By rewriting equations (11) and (12) we obtain

$$\frac{RT}{600} \ln \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{0.24}{600} \frac{2}{0} + \frac{E_h}{600} - n \dots(13)$$

$$\frac{\text{HLB} - 7}{0.475} = \frac{(\text{hydrophilic group numbers})}{0.475} - n \dots(14)$$

From these equations we obtain the first set of three relations (true only for $A_1 = A_2$), showing that the hitherto empirical HLB system rests on a firm kinetic basis

$$\ln(\text{Rate}_2/\text{Rate}_1) = 2.2 (\text{HLB} - 7) \quad \dots (15)$$

$$\text{hydrophilic group number for single hydrated group} = E_n/1260 \quad \dots (16)$$

$$\text{hydrophilic group number for charged group} = 1.9 \times 10^{-4} \phi_0^2/\phi_0 \quad \dots (17)$$

According to equation (15), neither a W/O nor an O/W emulsion is favoured if either $\text{HLB} = 7$, or if ϕ_0 is very small for an emulsifying agent of any HLB. For a typical O/W emulsifying agent, $\text{HLB} = 11$, $\phi_0 \sim 1$, and so $\text{Rate}_1 = 10^{-4} \text{Rate}_2$. Comparison of equation (15) with experiment for n-alcohols is made in Table IV, columns 3 and 4.

Equation (16) shows that for hydrated groups the HLB group numbers (Table III) should be proportional to the energy barrier to coalescence (Figure 1) set up by the water which is firmly bound to hydroxyl or ester groups on the surface active agent. Thus, for a single hydroxyl group of group number 1.9, E_n is calculated from equation (16) to be $1260 \times 1.9 = 2400$ cal. This is rather less than the 4000 cal estimated above for the work of complete dehydration of an -OH group. The relation of HLB to hydration also explains the observed correlation^{15,16} of HLB with the cloud point, the temperature to which a 5 per cent solution of detergent may be heated before it becomes turbid: this temperature is related¹⁶ to the dehydration energy of the detergent. In the sorbitan ring the group-number of a hydroxyl group (Table III) and therefore the hydration are less than for a free hydroxyl group, presumably due to steric effects. The higher group number of an ester linkage to the sorbitan ring is possibly due to an orientation factor in addition to hydration.

According to equation (17) the HLB group number of a charged group (e.g. sulphate or sulphonate) depends on ϕ_0 and ϕ_0 : the potential ϕ_0 is determined by the total electrolyte concentration and ϕ_0 . Thus the contribution of a charged group to the HLB of an anionic or cationic surface active agent is not strictly constant. For sodium lauryl sulphate the hydrophilic group contribution is calculated from equation (17) to be 35 if $\phi_0 = -230$ mV and $\phi_0 = 0.29$. Hence the HLB for sodium lauryl sulphate is calculated (equation (12)) to be 36. The experimental value^{15,32} (Table II) lies between 35 and 40, but since the exact conditions obtaining are unspecified, more precise comparison is not possible.

Distribution of emulsifier between oil and water (Bancroft rule)

The distribution of (say) an alcohol between oil and water is determined by the free energy of transfer of the molecule from water to oil, $G_{w \rightarrow o}$

$$G_{w \rightarrow o} = -RT \ln(c_o/c_w) \quad \dots(18)$$

where c denotes emulsifier concentration, and subscripts o and w refer to oil and water. The work of transfer, $G_{w \rightarrow o}$, is made up of terms from the hydrophilic and lipophilic parts of the molecule, the former energy being $+3200$ cal mole⁻¹ for an -OH group³¹, and the latter -800 cal mole⁻¹ for a -CH₂- group in a hydrocarbon oil^{33,34}. Thus, for an alcohol

$$G_{w \rightarrow o} = +3200 - 800n$$

where, as before, n is the number of -CH₂- groups in the molecule. In general

$$G_{w_o} = G_{w_o}(\text{hydrophilic groups}) - 800 n \quad \dots(19)$$

Combining equations (18) and (19) we find

$$\frac{RT}{800} \ln \frac{c_w}{c_o} = \frac{G_{w_o}(\text{hydrophilic groups})}{800} - n \quad \dots(20)$$

This may be compared with the result of the kinetic treatment, equation (13) above, from which the second set of relations follow if $A_1 = A_2$ and if emulsion type and emulsifier partition can thus be directly related

$$\frac{\text{Rate}_2}{\text{Rate}_1} = (c_w / c_o)^{0.75} \quad \dots(21)$$

$$E_h = 0.75 G_{w_o} (\text{uncharged hydrophilic group}) \quad \dots(22)$$

$$0.32 \frac{z}{o} / = G_{w_o} (\text{charged hydrophilic group}) \quad \dots(23)$$

The Bancroft rule is implied in equation (21): additives preferentially soluble in water stabilize O/W systems (cf. relation (7) above), and vice versa. This hitherto empirical rule therefore also has a kinetic basis, and will be obeyed if equations (22) and/or (23) are true. Equation (21) is tested for n-alcohols in Table IV (columns 4 and 5).

Table IV

| <i>Emulsion stabilizer (alcohols)</i> | HLB | $\frac{\text{Rate}_2}{\text{Rate}_1}$ (calc. from eq. (15) with $\frac{z}{o} = 1$) | $\frac{\text{Rate}_2}{\text{Rate}_1}$ (observed) | $\frac{c_w}{c_o}^{0.75}$ (data from Hutchinson ³⁵) | $7 + 0.36 \ln \frac{c_w}{c_o}$ (data from Hutchinson ³⁵) |
|---------------------------------------|-----|---|--|--|--|
| <i>Methanol</i> | 8.4 | 23 | 30 | 22 | 8.5 |
| <i>Ethanol</i> | 7.9 | 8 | 11 | 8 | 8.0 |
| <i>n-Propanol</i> | 7.4 | 2.7 | 4 | 2.8 | 7.4 |
| <i>n-Butanol</i> | 7.0 | 1 | 1 | 1 | 7 |

Emulsions were made by hand-shaking test-tubes containing petrol-ether and water and stabilizer. Rate measurements were made by timing with a stop-watch the breaking of the unstable emulsions on each side of the interface.

Equation (22) predicts that E_h , the work of removing the water from (say) a hydroxyl group, must be of the same magnitude as the total work done in taking the group from water to oil: this is indeed true for non-polar oils such as decane, in which the interaction between oil and a hydroxyl group is small. Thus for non-ionic emulsifiers ($\frac{z}{o} = 0$) equations (13) and (20) are strictly comparable, and so the Bancroft rule should always be obeyed if $A_1 = A_2$ and the oil is non-polar.

The Bancroft rule (as implied in equation (21)) will also be valid for ionic emulsifying agents such as sodium lauryl sulphate if equation (23) is correct. It is, however, clear from the considerations in Appendix II that equation (23) holds only as regards orders of magnitude: when c_o is low (small concentrations of emulsifier, high salt concentration) equation (23) will no longer be accurate-and so neither will the Bancroft rule.

HLB and the Bancroft rule

If we compare equation (20) with the HLB equation (14) above, we obtain the third set of fundamental relations

$$(HLB - 7) = 0.36 \ln (c_w / c_o) \quad \dots(24)$$

$$\frac{\text{Hydrophilic group number for single hydrated group}}{1680} = \frac{G_{w-o}(\text{uncharged hydrophilic group})}{1680} \quad \dots(25)$$

$$\frac{\text{Hydrophilic group number for charged group}}{1680} = \frac{G_{w-o}(\text{charged hydrophilic group})}{1680} \quad \dots(26)$$

If equations (25) and (26) are correct, then equation (24) will hold: i.e. the HLB and distribution characteristics of emulsifiers can always be related. The Bancroft rule and HLB are thus equivalent, according to equation (24) so that if the emulsifier is preferentially soluble in water, $HLB > 7$, and vice versa. We can see at once that equation (25) is valid for the simple alcohols, since $G/1680$ is $3200/1680 = 1.9$ for an OH group, which is precisely its group number (Table III).

Hence equation (24) should hold strictly for non-ionic emulsifiers. That this is indeed so is clear from Table IV, columns 2 and 6. *In general, equation (25) allows us to predict the group number of an uncharged hydrophilic group from the free energy change in passing from water to a hydrocarbon oil:* thus for the -OH group in n-alcohols, $G_{w-o} = + 3200$ cal, and hence the HLB group number calculated by equation (25) is 1.9.

The lack of success attending previous attempts¹⁵ to correlate HLB values with the distribution of non-ionic emulsifying agents between oil and water may well have been due to dissolved water: to test equation (24) the emulsifying agent should be dissolved in the oil under conditions such that the oil remains non-polar, i.e. no dissolved or solubilized water must be present. Similarly in the aqueous phase, there should be no micelles nor dissolved nor solubilized oil.

Equation (26) will be an approximation, since it follows from equations (17) and (23), the latter being correct only as regards order of magnitude. The application of equation (26) is discussed in Appendix II.

The use of two emulsifying agents

Schulman and Cockbain²⁵ have given a detailed analysis of the importance of a long-chain alcohol in promoting the stability of an O/W emulsion. According to equation (3), taking $\phi_o = - 175$ mV for the emulsion stabilized by detergent alone, $Rate_1 = 10^{-5} A_1$. Now, if cetyl alcohol is present, the potential ϕ_o will be effectively unaltered, but for the alcohol $\phi_h = 0.5$ and $E_h = 2400$ cal. Hence, by equation (3), $Rate_1 = 10^{-6} A_1$, so the emulsion is in this case ten times more stable than without the long-chain alcohol.

Breaking and inversion of emulsions

An O/W emulsion will break or invert whenever $Rate_1$, as defined by equation (3), becomes large. Whether in fact breaking or inversion actually occurs will depend on the stability of the inverse system: if this unstable and $Rate_2$ of equation (4) is large, the emulsion will break. If, however, $Rate_2$ is small, the emulsion will invert. This is illustrated

in Figure 5. Practical limits to the terms large and small are $10^{-2}A$ (coalescence occurring within an hour) and $10^{-5}A$ (emulsion stable for several months).

Consider as an example the *breaking of an emulsion of paraffin oil* in water stabilized by a long-chain sulphate or by laurate. Initially we might have $\phi_0 = -175$ mV, $\phi = 0.4$, so that $\text{Rate}_1 = 10^{-5} A_1$ and $\text{Rate}_2 = 10^{-2} A_2$. After the addition of 0.3 M NaCl, however, ϕ_0 is reduced to about -100 mV and ϕ is increased slightly to 0.45 because of the reduced repulsion; Rate_1 is now increased to the large value of $2 \times 10^{-2} A_1$, whereas Rate_2 is still quite large (because n is only 11 or 12) being about $10^{-2} A_2$. Thus after the addition of the NaCl the conditions for *emulsion breaking* are satisfied (sequence (a), (b), (c), (d) of Figure 5), in accord with experiment²⁴. We may also note that further additions of sodium chloride cannot invert the emulsion: with a C_{11} chain Rate_2 will never become sufficiently small. This is also in accord with experiment³⁷.

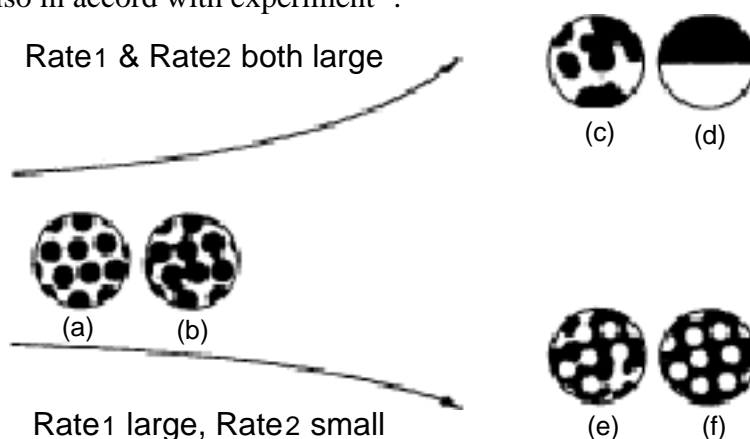


Figure 5. Diagrammatic representation of breaking and inversion of emulsions. The dark liquid is oil and the white liquid is water. The breaking of this O/W emulsion occurs because Rate_1 is large, and continues to phase separation if Rate_2 is also large, as in the sequence (a), (b), (c), (d).

If, however, Rate_1 is small, the sequence leads to inversion (a), (b), (e), (f).

This method of representation has been adapted from Sutheim³⁶ and from Schulman and Cockbain²⁵, and can be equally applied to W/O emulsions

The breaking of W/O emulsions with sodium oleate or 'Teepol'^{20,21} also supports the theory. A W/O emulsion will break when Rate_2 becomes great, while Rate_1 also remains large. Now if the surface is well covered (~ 1) with (say) calcium oleate, ϕ -monostearin³⁸ or asphaltic material^{20,21}, detergent or soap must be added in sufficient quantity to displace this: due to electrical repulsion ϕ is lower in this new interfacial film and so Rate_2 is greater now, being perhaps $10^{-2} A_2$ instead of (say) $10^{-7} A_2$ as in the original emulsion. At the same time Rate_1 remains large, changing from about A_1 to about $10^{-2} A_1$ (assuming there is 0.4 N salt in the aqueous phase).

Inversion of an O/W emulsion will occur when Rate_1 becomes large while Rate_2 is small. Consider, for example, an emulsion of water in oil stabilized with a longer chain compound than before, such as sodium stearate. Initially, we might have $\phi = 0.4$, $\phi_0 = -175$ mV so that again $\text{Rate}_1 = 10^{-5} A_1$. Rate_2 is now $10^{-3} A_2$. After the addition of 0.5 M NaCl, however, $\phi = 0.6$ and $\phi_0 = -90$ mV, so that Rate_1 is increased to $0.5 \times 10^{-2} A_1$ while because n is now as high as 17, Rate_2 calculated by equation (4) has the low value of

$3 \times 10^{-5} A_2$. Since in this system $Rate_2$ is so small, inversion will occur³⁷ (sequence (a), (b), (e), (f), of Figure 5) in accord with the general principles above. We may observe that $Rate_2/Rate_1 \ll 1$ in the system containing added salt.

The inversion will be more complete, of course, if calcium or other ions forming undissociated soaps⁵ are present (see also Appendix II). If all the soap in the system is calcium soap, the electrostatic potential ψ_0 in a stearate stabilized emulsion will be practically zero, so that $Rate_1 \sim A_1$ although, since $\psi_0 \sim 1$, for the condensed interfacial film of calcium soap, $Rate_2 = 10^{-7} A_2$. Here we have the possibility of a stable W/O emulsion, as is widely known from practical experience⁵.

Emulsion breaking or inversion can be effected by adding sufficient of any surface active agent to displace the adsorbed film and stabilize, weakly or strongly respectively, the opposite type of emulsion.

APPENDIX I

When two charged surfaces, immersed in a solution of electrolyte, approach, the repulsive potential varies approximately as ψ_0^2 , whether the surfaces are flat or curved^{39,40}. Here ψ_0 is the electrostatic potential of each surface. The constant of proportionality depends on the radius of curvature of the approaching surfaces, but since liquid drops nearly in contact may be expected to flatten considerably or even become slightly concave^{23,41}, the radius of curvature to be used for emulsion drops may be far from the actual drop radius. In these circumstances we assume that the radius of curvature of the adjacent charged surfaces is constant for emulsion drops of the order 1μ in diameter, and this constant is determined empirically.

The possibility of long-range attraction between oil drops in water must also be considered, and if this is important both the constant of attraction, A , and the Debye-Hückel thickness $1/\kappa$ must be included^{40,42} in the constant of proportionality between repulsive potential and ψ_0^2 . Recent work⁴³, however, suggests that A may be 20 times smaller than it was formerly believed to be, and accordingly here we do not, as a first approximation, include A and $1/\kappa$ in the calculation.

If we write for the coalescence of charged emulsion drops

$$Rate_1 = A_1 \exp\left(-B \frac{\psi_0^2}{RT}\right)$$

we may obtain B empirically from Lawrence's kinetic experiment⁴⁴. For sodium oleate stabilized emulsions, if A_1 is given by the Smoluchowski theory, $-B \frac{\psi_0^2}{RT} = -11.2$. If there is one electronic charge per 45 \AA^2 , the Gouy equations⁴⁰ give $\psi_0 = 165 \text{ mV}$, whence $B = 0.24$.

From Pethica and Few's data on unstable emulsions²⁴ we have similarly $-B \frac{\psi_0^2}{RT} = -6$, where ψ_0 is -123 mV according to the Gouy theory, when 0.4 N NaCl is present, whence $B = 0.23$.

Lawrence and Mills⁴⁴, in experiments on oil drops in water without additives, found that the system was about 750 times more stable than according to the Smoluchowski theory. The ψ_0 -potential of oil drops in water is about -70 mV , due to adsorption of hydroxyl ions,

and hence, using the relation⁴⁵ $\phi = 0.55 \phi_0$, $\phi_0 = -127$ mV. Hence for the oil drops in water $-B \phi_0^2/RT = -6.6$, whence $B = 0.24$.

We have used throughout this paper a value of 0.24 for B. In general, a 10-fold increase in uni-univalent electrolyte concentration will decrease ϕ_0 numerically by 60 mV, and so will greatly decrease the stability of an O/W emulsion.

APPENDIX II

The free energy of transferring an ionic group from water to oil depends on the radius of the ion, and, according to the Born equation, is about 36,000 cal for the unhydrated sulphate group. For the counter-ion (e.g. Na⁺ or K⁺) the energy will be higher still, so the total will be of the order 80,000 cal. This cannot depend on ϕ : equation (23) cannot therefore be exact. However, if $\phi_0 = -230$ mV, $\phi = 0.29$, the left-hand side is about 60,000 cal. Thus equation (23) is correct as regards orders of magnitude in salt-free solutions of fully ionized detergents. If now NaCl is present, ϕ_0 may be considerably less, while ϕ is but slightly affected, so that the equation will no longer be correct even in order of magnitude. The inversion of O/W emulsions by addition of NaCl as discussed above shows that though the ionic stabilizer may still be preferentially water-soluble, a W/O emulsion may result⁴⁶. If sparingly dissociated calcium salt is formed, ϕ_0 will be very low, and equation (22) should be used in place of equation (23).

Equation (26) can be only approximately correct, even for solutions of detergents in distilled water. Taking $\phi = 80,000$ cal, we obtain the hydrophilic group number for the sodium sulphate group to be 47. Equation (17) shows, however, that this group number may vary widely, depending on emulsifier concentration, the concentrations of added salts, particularly if these are polyvalent. Under such conditions equation (26) is not valid.

REFERENCES

- ¹ Ostwald, *Kolloidschr.* **6**, 103, 1910
- ² Cheesman and King, *Trans. Faraday Soc.* **34**, 594, 1938
- ³ Andreas, *J. chem. Educ.* **15**, 523, 1938
- ⁴ Isemura and Kimura, *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **6**, 54, 1948
- ⁵ Clayton, *The Theory of Emulsions and their Technical Treatment*, 5th ed. By C. G. Sumner, London, 1954
- ⁶ Dickinson and Iball, *Research, Lond.* **1**, 614, 1948
- ⁷ Robertson, *Kolloidschr.* **7**, 7, 1910
- ⁸ Stamm, *J. phys. Chem.* **30**, 998, 1926
- ⁹ Bancroft, *J. phys. Chem.* **17**, 514, 1913 10
- ¹⁰ McBain, *Colloid Science*, Boston, 1950
- ¹¹ Cassel, *Nature, Lond.* **137**, 405, 1936
- ¹² Cassel, *J. phys. Chem.* **42**, 475, 1938
- ¹³ Griffin, *J. Soc. Cosmet. Chem.* **1**, 311, 1949
- ¹⁴ Griffin, *Emulsions, Encyclopedia of Chemical Technology*, ed. by Kirk and Othmer, **5**, 692 New York, 1950,

- ¹⁵ Griffin, *J. Soc. Cosmet. Chem.* **5**, (4), 1954
- ¹⁶ Griffin, Official Digest (Fed. Paint varnish Production Clubs), June, 1956
- ¹⁷ Rehbinder and Wenström, *Kolloidschr.* **23**, 145, 1930
- ¹⁸ Davies, J. T. *Perf. Essential Oil Record*, **43**, 338, 1952
- ¹⁹ Cockbain and McRoberts, *J. Colloid Sci.* **8**, 440, 1953
- ²⁰ Lawrence, *Chem. & Ind. (Rev.)* **39**, 615, 1948
- ²¹ Lawrence and Killner, *J. Inst. Petrol. Tech.* **34**, 821, 1948
- ²² Cockbain, *Trans. Faraday Soc.* **48**, 185, 1952
- ²³ Gillespie and Rideal, *Trans. Faraday Soc.* **52**, 173, 1956
- ²⁴ Pethica and Few, *Disc. Faraday Soc.* **18**, 258, 1954
- ²⁵ Schulman and Cockbain, *Trans. Faraday Soc.* **36**, 651, 661, 1940
- ²⁶ van der Waarden, *J. Colloid Sci.* **5**, 317, 1950
- ²⁷ van der Waarden, *J. Colloid Sci.* **6**, 443, 1951
- ²⁸ Mackor, *J. Colloid Sci.* **6**, 492, 1951 ; Mackor and van der Waals, *J. Colloid Sci.* **7**, 535, 1952
- ²⁹ Archer and La Mer, *Ann. N.Y. Acad. Sci.* **58**, 807, 1954
- ³⁰ *Atlas Surface Active Agents*, Atlas Powder Co., Delaware, U.S.A., 1950, p 22
- ³¹ Davies, unpublished work
- ³² Griffin, private communication
- ³³ Crisp, *Surface Chemistry*, p 65. Butterworth, London, 1949
- ³⁴ Davies, *Trans. Faraday Soc.* **48**, 1052, 1952
- ³⁵ Hutchinson, *J. phys. Chem.* **52**, 897, 1948
- ³⁶ Suthem, *Introduction to Emulsions*, New York, 1946
- ³⁷ Tartar, Lothrop and Pettengill, *J. phys. Chem.* **34**, 373, 1930
- ³⁸ Jellinek and Anson, *J. Soc. chem. Ind.* **68**, 108, 1949
- ³⁹ Derjaguin, *Trans. Faraday Soc.* **36**, 203, 1940
- ⁴⁰ Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids*, Amsterdam, 1948
- ⁴¹ Dejaguin and Kussakov, *Acta phys.-chim. U.R.S.S.* **10**, 25, 1939
- ⁴² Derjaguin, *Trans. Faraday Soc.* **36**, 730, 1940
- ⁴³ Derjaguin *et al.*, *Disc. Faraday Soc.* **18**, 24, 1954
- ⁴⁴ Lawrence and Mills, *Disc. Faraday Soc.* **18**, 98, 1954
- ⁴⁵ Davies and Rideal, *J. Colloid Sci. Supplement* **1**, 1, 1954
- ⁴⁶ Blakey and Lawrence, *Disc. Faraday Soc.* **18**, 268, 1954