The Probable Existence of Acid Aluminium Di-soaps

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The following paper gives a survey of the mechanisms by which fatty acid can be taken up by aluminium di-soap. The possible phase equilibria between a fatty acid solution and an aluminium soap solid are deduced thermodynamically. The relationships thus obtained are compared with experimental results of Coe, Mysels and Smith [1], and conclusions are drawn about the existence of an acid aluminium di-soap.

Precipitation of aluminium soaps from alkali soap (denoted NaL) solutions results in products of indefinite composition with an aluminium content varying from that of the di-soap $AlOHL_2$ to that of the tri-soap AlL_3 [2,3]. By Soxhlet extraction of these products with an anhydrous organic solvent, which dissolves only the fatty acid, aluminium di-soap with the theoretical composition is obtained [4]. Consequently a true tri-soap AlL_3 had not been formed. The existence of an aluminium di-soap is shown by X-ray analysis [5].

Most organic liquids dissolve or swell aluminium di-soaps, but a few organic solvents such as acetone and some paraffin hydrocarbons do not dissolve aluminium soaps. Coe, Mysels and Smith [1] examined the equilibrium between stearic acid dissolved in acetone or isooctane and a solid consisting of aluminium stearates. They found a relationship between the stearic acid content of the solution and the mole ratio HL/Al in the solid, indicating that fatty acid was taken up by the di-soap. Thus the possible existence of an acid aluminium di-soap $AlOHL_2HL$, overlooked before [6-8], is indicated. Compare this with the established existence of acid alkali soaps $aNaLbHL$ (a and b being integers) [9], which release their excess fatty acid on extraction [10]. It must be borne in mind that there is no principal difference between an acid di-soap $AlOHL_2HL$ and a compound represented by AlL_3H_2O, because neither of these can release water if the anhydrous tri-soap AlL_3 does not exist.

In the present paper the equilibrium between a fatty acid and its aluminium soaps is studied theoretically on the basis of possible phase compositions of the soap solid. The presence of an anhydrous solvent, capable of dissolving the fatty acid but inert to the aluminium soaps, is assumed. Relations between the fatty acid concentration in the solution and the over all composition of the soap solid are deduced, with the latter variable as the independent one. The total composition of the solid will be given as the amount of fatty acid exceeding di-soap composition and expressed by the mole ratio $HL/AlOHL_2$ ($= x$). Dissolved fatty acid is represented by its activity $a_{HL(l)}$. The pure compounds have unit activity (standard state) and ideal solutions are assumed. Differences caused by the use of different solvents are consequently eliminated. Common symbols are used, (s) and (l) denoting solid and liquid phase.

POSSIBLE PHASE COMPOSITIONS OF THE SOLID

A. The solid consists of aluminium di-soap and fatty acid, according to the following phase behaviour

    1) fatty acid and di-soap form two separate phases
    2) fatty acid and di-soap form a solid solution
    3) fatty acid is adsorbed on the solid di-soap.

A partition equilibrium for the fatty acid exists corresponding to $HL(s) \rightleftharpoons HL(l)$.

B. The solid consists of aluminium di-soap and acid aluminium di-soap, where
    1) di-soap and acid di-soap form separate phases
    2) di-soap and acid di-soap form a solid solution.

The concentration of fatty acid in solution is determined by the equation $AlOHL_2HL(s) \rightleftharpoons AlOHL_2(s) + HL(l)$

Deduction of phase equilibria.
A) Solid consisting of $AlOHL_2$ and HL according to $HL(s) \rightleftharpoons HL(l)$

    1) *The solid components form separate phases.* The solution will be saturated as soon as the fatty acid content of the solid is raised above that of the di-soap, giving the relation $a_{HL(l)} = 1$ as represented by curve a in Fig. 1

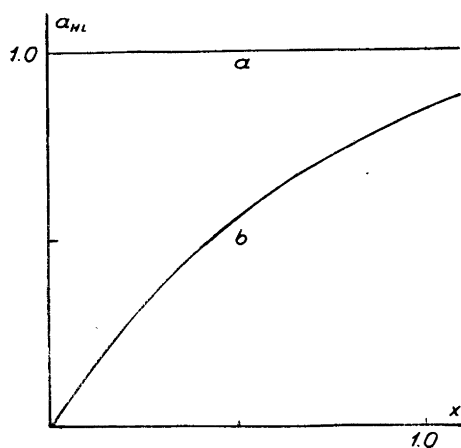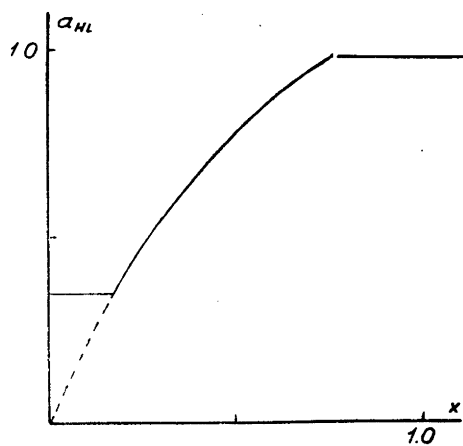Fig. 1. Solid consisting of HL and $AlOHL_2$ (a) as separate phases, (b) in a solid solution.

Fig. 2. Solid solution of HL and $AlOHL_2$ at lower limited mutual solubility.

2) *The solid components form a solid solution.* It can easily be shown that in this case $a_{HL(s)} = K \dfrac{n_{HL}}{n_{AlOHL_2} + n_{HL}} = a_{HL(l)}, K$ being a constant. This simplifies to the relation $a_{HL(l)} = \dfrac{K \cdot x}{1 + x}$ represented by curve b in Fig. 1. In case of lower mutual solubility the relationship depicted in Fig. 2 represents the phase equilibrium.

3) *Adsorption of fatty acid on aluminium di-soap.* Applying Langmuir's concepts the number of adsorbed moles fatty acid per mole di-soap will be

$$x = \frac{p \cdot a_{HL(l)}}{1 + q \cdot a_{HL(l)}} \quad (p \text{ and } q \text{ being constants})$$

giving
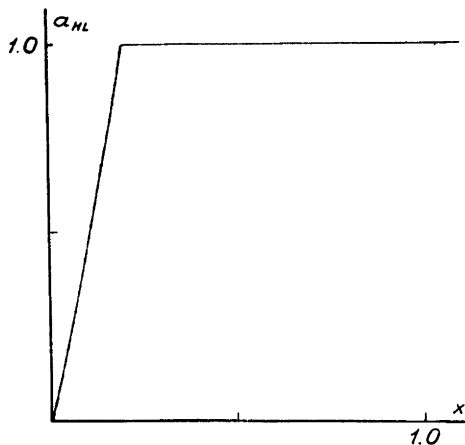
$$a_{HL(l)} = \frac{k_1 \cdot x}{(1 - k_2 x)}$$

The case is shown in Fig. 3.
If Freundlich's equation is applied similar results will be obtained.

B) Solid consisting of di-soap and acid di-soap according to

$$AlOHL_2HL(s) \rightleftharpoons AlOHL_2(s) + HL(l)$$

Fig. 3. Adsorption of HL on AlOHL$_2$.

1) *The solid components form separate phases.* Then the equilibrium constant is $a_{HL(l)} = K$ where $K < 1$. The relationship is represented by the line EFGH in Fig. 4.

2) *The components form a solid solution.* The activities of the two components are

$$a_{AlOHL_2HL(s)} = \frac{p \cdot n_{AlOHL_2HL}}{n_{AlOHL_2HL} + n_{AlOHL_2}}$$

$$a_{AlOHL_2(s)} = \frac{q \cdot n_{AlOHL_2}}{n_{AlOHL_2} + n_{AlOHL_2HL}}$$

p and q being constants. Equilibrium requires:

$$K_1 = \frac{a_{HL(l)} \cdot a_{AlOHL_2(s)}}{a_{AlOHL_2HL(s)}}$$

Thus

$$a_{HL(l)} = \frac{K \cdot x}{(1 - x)}$$

The equilibrium constant K determines the highest possible solubility of AlOHL$_2$HL in AlOHL$_2$. Curve ADFGH or, in case of a limited mutual solubility curve CBDFGH, in Fig 4 represents this case. If AlOHL$_2$HL exists only in solid solution with AlOHL$_2$ but not in a pure state, the phase equilibrium is represented by Fig 5, where fatty acid exists as a solid phase within the range AB.
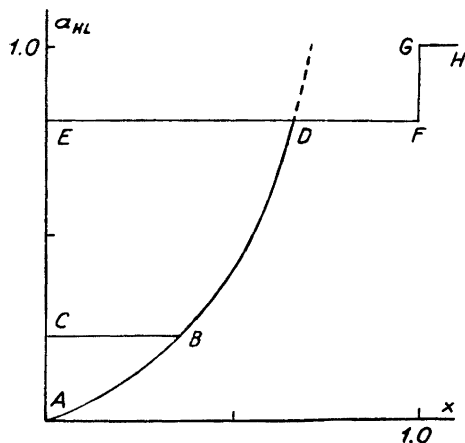
Fig. 4. Solid consisting of $AlOHL_2$ and $AlOHL_2HL$.
Line EFGH: as separate phases,
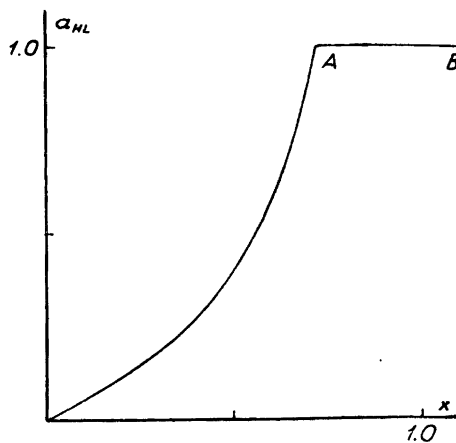Line ADFGH or CBDFGH: in a solid solution.

Fig. 5. Solid solution of $AlOHL_2$ and $AlOHL_2HL$, if the latter component does not exist in a pure state.

The same relation can be obtained by a statistical treatment, simultaneously giving a good picture of the structure of the single phase system di-soap— acid di-soap. Let us postulate that one molecule fatty acid can be bound as an upper limit to each di-soap molecule in the single phase system. Thus a solid solution of acid di-soap in di-soap is formed.

Then assuming fatty acid is released with the rate $v_1 = R_1 x$ and combined with the rate $v_2 = R_2 (1 - x) a_{HL(l)}$, R_1 and R_2 being constants, we find at equilibrium $v_1 = v_2$ and again: $a_{HL(l)} = \dfrac{K \cdot x}{(1 - x)}$.

COMPARISION WITH EXPERIMENTAL RESULTS ON ALUMINIUM STEARATES

Coe, Mysels and Smith [1] present the experimentally obtained relationship for stearic acid and aluminium stearate at 30° C in the same way as in our figures. From a comparison it is obvious that either sorption of fatty acid on di-soaps (A : 3) or a limited formation of acid di-soap (B : 2) may account for their results. The two corresponding equations differ only by the presence of a constant k_2 in the denominator of the equation A : 3. Table 1 shows the excellent agreement with both formulae assuming in the case A : 3 that k_2 is unity. However, the high value reached for the ratio of adsorbed substance to adsorbent makes it improbable that true surface adsorption takes

Table 1. Comparison of experimental results on the system aluminium stearate — stearic acid at 30° C with the equation $a_{HL(l)} = \dfrac{K \cdot x}{(1-x)}$ *(Case B : 2).*

$a_{HL(l)}$	x observed *	K **	x calculated ***
1.00	0.64	0.56	0.67
0.90	0.63	0.53	0.64
0.80	0.60	0.53	0.61
0.70	0.58	0.51	0.58
0.60	0.55	0.49	0.55
0.50	0.51	0.48	0.50
0.40	0.46	0.47	0.44
0.30	0.38	0.49	0.38
0.20	0.29	0.49	0.29
0.10	0.17	0.49	0.17
		Mean 0.50	

* Values taken from Fig. 1 of Coe, Mysels and Smith [1].
** K values calculated from $a_{HL(l)}$ and x values observed.
*** Calculated using obtained mean value $K = 0.50$.

place. Consequently the best explanation for the experimental results is that the aluminium stearate solid consists of AlOHSter$_2$HSter and AlOHSter$_2$. These components then form a one phase system up to an acid content of 0.67 mole HSter per mole AlOHSter$_2$ corresponding to 0.33(AlOHSter$_2$) 0.67 (AlOHSter$_2$HSter), very close to 3AlOHSter$_2$2HSter.

At higher total acid content in the solid the activity of fatty acid in the solvent should be constant. This acivity must be less than unity if AlOHL$_2$HL is present here as a pure phase (Fig. 4). Theoretically, it can reach unity, then making it difficult to draw conclusions concerning this region of the solid phase. The experiments with stearic acid may point to the existence of a pure stearic acid phase in this region together with a phase of 3AlOHSter$_2$2HSter.

Further research will be carried out on the aluminium abietate — abietic acid system.

SUMMARY

By thermodynamic treatment phase equilibria between fatty acid solutions and a solid of aluminium soaps are deduced on the basis of possible phase compositions of the solid. By comparison with earlier published experimental work evidence is obtained for the existence of an acid aluminium di-stearate

with a composition varying from AlOHSter$_2$ to a compound close to 3Al(OH)Ster$_2$2HSter, which can be interpreted as a solid solution of di-stearate AlOHSter$_2$ and acid di-stearate AlOHSter$_2$HSter.

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