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Association Equilibria in Solutions of Alkali Salts of Straight Chain Acids. I. Salts of Monocarboxylic Acids

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Association in soap solutions is treated as a reversible chemical reaction. The calculations are based on solubilization data and the effect of an excess of sodium ions on the critical concentration. For the association energy per mole of soap at 20° C an expression $\Delta G_{ass} = 620\ \eta + 3\ 680$ cal, is derived where η is the number of methylene groups in the soap molecule.

The association which takes place in solutions of association colloids must be considered a reversible chemical process, and should hence comply with the law of mass action. This necessity has frequently been stressed by investigators, for example, McBain, Hartley, Stauff, Lamm and Hobbs [1-8].

Owing to the fact that very little is known with certainty about the composition and structure of the micelles that are the products of the association, it has been difficult to apply the law of mass action. Also in the formal respect the treatment will be complicated since a very large number of reacting species are involved in micelle formation. Further complications are provided by the stepwise nature of the association process, and by the fact that various equilibria dominate in different concentration ranges.

It is perhaps possible to overcome the last-mentioned difficulties by applying the core and links principle of Sillén [9]. In the following, however, we shall in applying the mass action law to the association process disregard the various intermediate stages of association and consider only the equilibrium between simple ions and the so-called small micelles. One of the main objectives will be to estimate the energy of association per mole of paraffin-chain ion on the basis of available experimental data.

Micelle formation in a soap solution is a reaction of the type:

$$\mathrm{nMe^+ + mL^- = (Me_n^+\ L_m^-)^{(m-n)^-}} \tag{1}$$

where m denotes the number of paraffin-chain ions in the micelle and n the number of counter-ions bound to the micelle. The equilibrium constant for the process is given by the expression

$$K = \frac{a_{\mathrm{mic}}}{(a_{\mathrm{Me^+}})^{\mathrm{n}}\,(a_{\mathrm{L^-}})^{\mathrm{m}}} = \frac{f_{\mathrm{mic}}[\mathrm{Me_n^+ L_m^-}]}{f_+^{\mathrm{n}}[\mathrm{Me^+}]^{\mathrm{n}}\,f_-^{\mathrm{m}}[\mathrm{L^-}]^{\mathrm{m}}} \tag{2}$$

where f_{mic} is the activity coefficient of the micellar particle and f_+ and f_- the activity coefficients of the free ions. The change in free energy per mole, *i. e.* the association energy of associated paraffin-chain ions, ΔG_{ass} will be

$$\Delta G_{\mathrm{ass}} = -\frac{RT}{\mathrm{m}} \ln \frac{f_{\mathrm{mic}}[\mathrm{Me_nL_m}]}{f_+^{\mathrm{n}}[\mathrm{Me^+}]^{\mathrm{n}} f_-^{\mathrm{m}}[\mathrm{L^-}]^{\mathrm{m}}} \tag{3}$$

We shall now attempt to modify this expression by taking into account known experimental data. In the expression the power of f_{mic} is unity and further the concentration of the micellar substance expressed in moles per litre is very low. We may then without any greater error take f_{mic} to be unity.

As Stauff and other investigators have pointed out, important information about the association equilibria is provided by the value of the critical concentration [3]. Ekwall and Harva and later Kolthoff have established that the activities of simple fatty acid ions remain practically constant in the concentration range above the CMC [10, 11]. As we have been able to show, conducted studies of the ability of association colloids to solubilize substances insoluble in water yield further information on the nature of the association process [12]. It is obvious, of course, that the solubilized substance influences the association process, but it is possible to choose for study a sparingly soluble substance which to only a limited extent participates in micelle formation, *i. e.* one that does not appreciably alter the CMC of the association colloid. A suitable compound appears to be *p*-xylene. As we have previously found, the solubilization power of the solution can in this case be considered a measure of the extent of micelle formation [12].

In Fig. 1 the solubility of *p*-xylene is plotted as a function of the sodium laurate concentration in aqueous solution at 20° C [12]. From the curve it is seen that the solubilized hydrocarbon has not appreciably altered the critical concentration, which is 0.026—0.028 M for the pure colloid. At laurate concentrations somewhat above this limit, the solubility curve rises linearly with the soap concentration. The rising linear part of the curve has its origin at a soap concentration of approximately twice the CMC. Also the corresponding plots for other paraffin-chain salts have the same form [12]. The intermediate curved region between the two linear parts is due to the fact that micelle formation is not complete with respect to micelle size and extent of micelle formation immediately above the CMC. A certain higher concentration of the micelle-forming substance is necessary to effect this. Since the concentration of the unassociated soap anion changes relatively little with increase in the total colloid concentration above the CMC, all of the compound introduced at this point must be incorporated in micelles. It is obvious that as soon as the solubilization curve becomes linear and the saturation capacity of the micelles attains a constant value, a concentration range is reached where the properties are largely determined by micelles with a definite composition and structure. [12–16] A similar view of the micelles in this range has been expressed earlier by Hartley and Lamm and quite recently by Stitger, who studied the dependence of the conductance on the colloid concentration [2, 4, 17].

The point where the total colloid concentration is three times the CMC lies in many cases well within the range where the solubility curve is linear

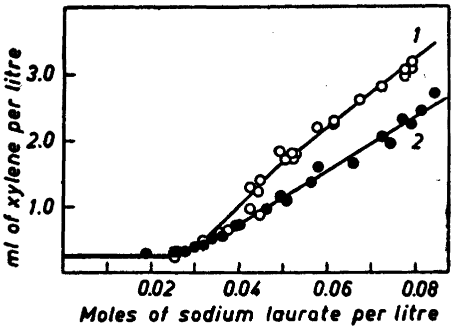

Fig. 1. The solubilization of p-*xylene in sodium laurate at 20° C (curve 1) and 40° C (curve 2). (Ekwall*[12]*.)*

(Fig. 1). We may therefore assume as a first approximation that the concentration of free soap anions is at this point equal to the CMC and that the rest of the soap, whose molecular concentration is twice the CMC, is in the micellar state. Thus when the total colloid concentration is three times the critical concentration, we have

$$[L^-] \approx C_{crit} \tag{4 a}$$

and

$$[Me_nL_m] \approx 2\,\frac{C_{crit}}{m} \tag{4 b}$$

Before we can make use of this latter expression, we require some knowledge of m. As mentioned above, the saturation capacity of the micellar substance gives some information about the size of the micelles, although strictly speaking the estimate obtained refers to micelles saturated with foreign substance [12]. If however, this substance is one that is incorporated between the palissade layers it is probable that the number of fatty acid ions per micelle is little changed in the solubilization process.

It will be seen below that a variation in m amounting to ± 50 % has a relatively small effect on the value of ΔG_{ass}. As long as m is greater than 10, the error made when we assume that the number of fatty acid anions is not altered in the solubilization process will not appreciably alter the final result. Studies of the roentgenographic structures, conductances, and other properties of the solutions have indicated that the solubilization of simple cyclic hydrocarbons brings about very small changes in the micelles [18, 19]. On the other hand, according to Booij, straight-chain aliphatic hydrocarbons seem to be at least partly built into the palissade layers [20]. Higher aromatic hydrocarbons possibly also effect marked changes in the micelle structure [21]. Compounds with polar groups participate actively in the formation of the micelles.

It has been found previously that the saturation capacity of oleate micelles (calculated from the linear part of the solubilization curve) for benzene is 186 ml, for toluene 183 ml and for *p*-xylene 177 ml per mole of micellar soap [12]. The volumes per mole of soap are approximately the same for these three substances, whereas when the amounts solubilized are expressed in moles per mole of micellar soap the values vary from 1.44 to 2.99. Similar results have been reported by Klevens [22]. This may be interpreted as evidence for the assumption that the volumes rather than the number of molecules solubilized are functions of the size of the micelles. In the following we shall assume that the micelles containing no foreign substance contain as many paraffin-chain ions as the micelles that are saturated with xylene.

In order to find the relation between the volume solubilized and the size of the micelle, it is necessary to make certain assumptions as to the structure of the micelle. We shall assume that the soap ions of the micelle form a monomolecular oriented layer around the dissolved hydrocarbon with their ionic groups pointed outwards towards the water and the hydrophobic paraffin-chains directed towards the solubilized hydrocarbon. By assuming the micelles containing hydrocarbon to be spherical in form and the area taken up by a paraffin-chain ion in the palissade layer equal to its cross-sectional area, it is possible to derive the relationship between the saturation capacity and the number of paraffin-chain ions in the micelle [12].

Let

k = saturation capacity of the micellar soap (Å^3 per mole)

q = cross-sectional area of the carbon chain of a soap molecule ($\approx$ 28 Å^2 according to roentgenographic measurements of Harkins [18])

r = radius of the enclosed sphere of xylene

N = Avogadro's number.

The number of paraffin-chain ions necessary to cover the sphere is

$$\mathrm{m} = 4\pi r^2/q \qquad (5\ \mathrm{a})$$

The volume of solubilized hydrocarbon is dissolved by m fatty acid ions. It therefore follows that

$$k = 4/3\ \pi r^3\mathrm{N}/\mathrm{m} \qquad (5\ \mathrm{b})$$

Eliminating r from equations (5 a) and (5 b), we obtain

$$\mathrm{m} = 36\pi k^2/q^3\mathrm{N}^2 \qquad (6)$$

This expression gives the number m of paraffin-chain ions in a micelle as a function of the saturation capacity k. Values of m calculated from this equation for several soaps are given in Table 1. The values calculated are obviously approximate and apply only to swollen micelles, but are of the same magnitude as the values obtained by Debye in a study of the light-scattering of pure solutions of alkyl trimethylammonium bromides and by Hutchinson in a study of sodium alkyl sulphates with alkyl groups of the same length [23, 24]. It is seen that the size of the micelles increases with the length of the paraffin-chain. It is clear that these considerations can apply only in the small micelle range; in higher concentration ranges, the conditions may be quite different [12-16, 25].

We draw attention again to the fact the even a relatively large error in the value of m does not significantly alter the value calculated for the energy of association of a soap molecule. This will be shown below (eq. 9 a).

The value obtained for the energy of association is however greatly dependent on the value assumed for the ratio n/m, the number of counter ions bound in the micelle. The value of the ratio n/m can be calculated from the shift in

*Table 1. The saturation capacity (*k *ml/mole) of the micellar soap for* p*-xylene and the number of paraffin-chain ions in soap micelles (m) calculated according to eq. 6* [12].

Soap	Temp.	k ml/mole	m
Sodium caprate	20° C	25	10
Sodium laurate	20° C	57	45
Sodium laurate	40° C	42.5	25
Sodium myristate	40° C	70	70
Sodium oleate	20° C	177	440
Sodium oleate	40° C	165	390
Sodium myristyl sulphate	40° C	115	190

the critical concentration caused by added alkali metal ions [26]. Eq. 2 can be written in the form

$$[\mathrm{L}^-] = \frac{[\mathrm{Me}_\mathrm{n}^+ \mathrm{L}_\mathrm{m}^-]^{1/\mathrm{m}}}{K[\mathrm{Me}^+]^{\mathrm{n}/\mathrm{m}}} \tag{7 a}$$

Let the total soap concentration be equal to the CMC. If we use the same method to determine the CMC of a soap under various conditions the critical concentration may be defined as the concentration where a certain fraction ε of the soap exists in the micellar state. We may now write equation 7 a in the form

$$(1-\varepsilon)C_\mathrm{crit} = \frac{(\varepsilon C_\mathrm{crit})^{1/\mathrm{m}}}{\mathrm{m}^{1/\mathrm{m}} K([\mathrm{Me}^+_\mathrm{tot}] - \mathrm{n}/\mathrm{m}\,\varepsilon C_\mathrm{crit})^{\mathrm{n}/\mathrm{m}}}$$

Since ε is small compared to 1 and $[\mathrm{Me}^+]_\mathrm{tot} \geqq [\mathrm{L}^-]$ in solutions containing excess alkali metal ions, this equation may, after taking logarithms, be written

$$\frac{\mathrm{m}-1}{\mathrm{m}} \log C_\mathrm{crit} = -\frac{\mathrm{n}}{\mathrm{m}} \log\,[\mathrm{Me}^+_\mathrm{tot}] - K' \tag{7 b}$$

When m is large, we obtain the equation given by Corrin

$$\log C_\mathrm{crit} = -\mathrm{n}/\mathrm{m} \log\,[\mathrm{Me}^+_\mathrm{tot}] - K' \tag{7 c}$$

Corrin has derived this equation by assuming that the micelles form a separate phase and hence that their activity in the solution remains constant [26].

Using the pinacyanol dye method, Corrin has determined n/m for a large number of paraffin-chain salts. For the potassium salts of fatty acids he found that the value of n/m is almost independent of the chain length, with an average value of 0.56. The present writers have by the same experimental method established that n/m = 0.56 for sodium caprate and 0.64 for sodium laurate at 20° C. The results of our measurements are shown in Fig. 2.

If n/m "gegenions" are bound per soap ion, it is possible to calculate the number of free metal ions at a total colloid concentration of 3 C_crit from eqs.

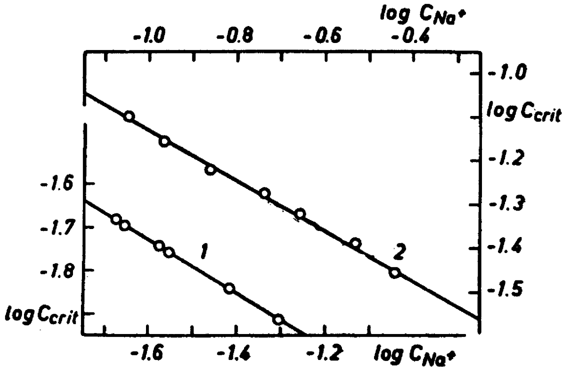

Fig. 2. Curve 1. The shift in CMC of sodium laurate solutions caused by added sodium chloride at 20° C. Curve 2. The shift in CMC of sodium caprate solutions caused by added sodium chloride at 20° C.

4 a and 4 b. The total concentration of metal ions is 3 C_{crit} and the concentration of bound metal ions is according to eq. 4 b equal to n/m 2 C_{crit}. Hence the concentration of free metal ions is

$$[\mathrm{Me}^+] = (3—2\mathrm{n/m})\ C_{\text{crit}} \tag{8}$$

When the equations 4 a, 4 b and 8 are substituted in 3, we have

$$\begin{aligned}\Delta G_{\text{ass}} = {} & \mathrm{R}T\ (\ln f_- + \ln C_{\text{crit}}) \\ & + RT\ \mathrm{n/m}\ [\ln f_+ + \ln\ (3—2\ \mathrm{n/m}) + \ln C_{\text{crit}}] \\ & — \frac{RT}{\mathrm{m}}\ (\ln f_{\text{mic}} + \ln 2\ C_{\text{crit}} — \ln \mathrm{m})\end{aligned} \tag{9 a}$$

As already noted, f_{mic} may be taken to be unity. If the colloid in question has a low critical concentration also f_+ and f_- can be set equal to unity. Further, if m is large, *i. e.* the micelles contain more than 10 paraffin-chain ions, the last term can also be omitted. Expression (9 a) will then become

$$\Delta G_{\text{ass}} = RT\ (1 + \mathrm{n/m})\ \ln C_{\text{crit}} + RT\ \mathrm{n/m}\ \ln\ (3—2\ \mathrm{n/m}) \tag{9 b}$$

This equation implies that the value of the association energy is mainly determined by the quantities ln C_{crit} and n/m, provided that the value of m is high. A qualitative interpretation is that the energy required to bring a charged group from the solution to the surface of a micelle with a charge of the same sign is primarily determined by the charge density on the micellar surface and not by the total charge on the micelle.

It is obvious that expressions 9 a and 9 b for the association energy are only approximate. The equations are based on the assumption that the activities of the simple paraffin-chain ions are constant above the critical concentration. This is not fully correct since it has been shown by activity measurements that already in the range below the CMC the activities of simple anions decrease slightly to a value that is definitely lower than the theoretical value[10]. At

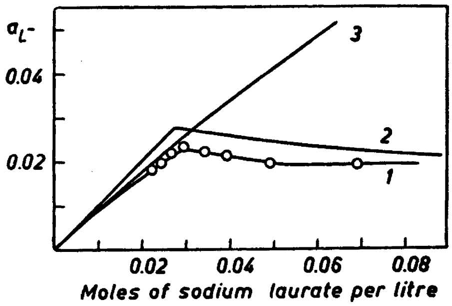

Fig. 3. Curve 1. The activity of laurate ions in sodium laurate solutions at 20° C (Ekwall and Harva[10]*). Curve 2. The concentration of laurate ions calculated according to Eq. 7 c. Curve 3. The mean activity of potassium acetate*[27]*.*

concentrations above CMC the activity of the simple anions decrease below the value at CMC owing to the fact that the rapid increase in the activity of free alkali ions shifts the association equilibrium in favour of micelle formation. This is clearly indicated by curve 1 in Fig. 3 which shows the variation of the activity of the anion in sodium laurate solutions[10]. For comparison, the variation of the mean activity in sodium acetate solutions is given in curve 3[27].

It is difficult to interpret the effect described above. By assuming the micelles to be a separate phase in the solution, it is, however, possible to estimate the variation of the anion activity with concentration in a laurate solution. In this case a_{L^-} is assumed to be given by the relation 7 c derived by Corrin[22].

$$\log a_{L^-} \approx - \mathrm{n/m} \log a_{Me^+} - k' \qquad (7\ c)$$

Curve 2 in Fig. 3 gives the activity of the free laurate ion calculated from this equation by assuming all activity coefficients to be unity. It will be noted that curves 2 and 1 in Fig. 3 differ slightly from each other, but are very similar in form.

If we assume that the difference between curves 1 and 2 in Fig. 3 at the concentration 0.030 M is due to the fact that about 10 % of the soap is bound as micelles and that the activities of the simple ions are approximately equal to the activities in potassium acetate solutions containing the same concentration of univalent ions as the soap solution, the application of eq. 7 c gives a curve that very closely follows the experimental values. From this it follows that eq. 7 c gives relatively good values for the activities of the ions in soap solutions.

By taking $f_{\pm}$ equal to unity and n/m = 0.56, calculation by successive approximation on the basis of eqs. 4 a, 4 b and 7 c shows that when the total soap concentration is three times the critical concentration $a_{L^-} \approx 0.74\ C_{crit}$. When this value is used to derive a value for the energy of association from 9 a, we obtain after simplification the equation (for 20° C)

$$\Delta G_{ass} = \frac{1\,340}{\mathrm{m}} \{\log \frac{\mathrm{m}}{2.26} + (\mathrm{m}-1) \log C_{crit}\} + 750 \log C_{crit} \qquad (9\ c)$$

All terms of the order of 10 cal were omitted in the derivation of this equation.

Table 2. The association energy (ΔG_{ass}) of the potassium and sodium salts of capric and lauric acid at 20° C calculated according to eqs. 9 a, 9 b and 9 c. The activity coefficients have been taken to be unity.

Soap	C_{crit} mole/litre	m	n/m	$\Delta G_{ass.}$ cal/mole (9 a)	(9 b)	(9 c)
Sodium caprate	0.097	10	0.56	−1 680	−1 920	−1 900
Sodium laurate	0.028	45	0.64	−3 120	−3 200	—
Potassium caprate	0.097	10	0.56	−1 680	−1 920	−1 900
Potassium laurate	0.028	45	0.56	−2 960	−3 050	−3 140

We have calculated from expressions 9 a, 9 b and 9 c the association energies of the sodium and the potassium salts of capric and lauric acids. The values of m employed are those given in Table 1, and have been used for both the sodium and potassium salts. The activity coefficients have been taken to be unity. The results are shown in Table 2. The values obtained for the two laurates differ very little from each other. For the association energies of the caprates, equations 9 a and 9 b give slightly different values. This is due to the low value of m used for the caprates.

It is known that the association energy is determined by the forces of attraction between the hydrocarbon chains in the soap molecules and between these and the water dipoles. These forces are proportional to the number of methylene groups in the carbon chain. On the other hand, repulsive forces act between the ionized groups on the micelle surface. These forces may be assumed to be independent of the length of the hydrocarbon chain and hence remain constant at least as long as the charge density on the micelle surface does not change. The charge density will remain the same if the ratio n/m remains constant. From these observations it follows that if we determine the association energies for a series of homologues and plot these as a function of the number of methylene groups, a linear plot $\Delta G_{ass} = a + \eta b$ should result, where η is the number of methylene groups in the paraffin-chain. The slope b gives the association energy per methylene group. The value b obtained on the basis of the calculated association energy of potassium laurate and caprate at 20° C is —620 cal per methylene group. This value is in satisfactory agreement with the value 1.08 RT derived by Shinoda [6]. The intercept a is + 3 680 cal at 20° C according to the values in Table 2. This energy is required to incorporate a charged carboxyl group in the micelle surface. It then follows that for the potassium soaps the association energy is

$$\Delta G_{ass} = -620\eta + 3\,680 \text{ cal} \tag{10}$$

It is here assumed, of course, that the hydrocarbon-chain is straight.

It is difficult to decide whether these values are correct. The energy liberated in the association is too small to be measured by calorimetric methods. In order to determine whether our reasoning is valid, we have calculated the association energy for several soaps from eq. 10. These values are given in the

Table 3. The association energy ΔG_{ass} and CMC of various soaps calculated on the basis of eq. 10 and eqs. 9 b and 9 c compared with experimental values of the CMC.[13,28,29,30]

Soap	$\Delta G_{\text{ass.}}$ cal./mole	CMC mole/litre	
		calc.	found
Potassium hexanoate	+ 580	1.5	1.5
—»— heptanoate	− 40	0.78	0.78
—»— octanoate	− 660	0.38	0.39
—»— nonanoate	−1 280	0.20	0.20
—»— undecanoate	−2 520	0.05	0.049
—»— tridecanoate	−3 760	0.012	0.0126
—»— tetradecanoate	−4 380	0.0075	0.0066
Sodium hexadecanoate	−5 620	0.0017	0.0032
—»— octadecanoate	−6 860	0.0004	
—»— oleate	−6 860	0.0004	0.0017−0.0008

second column of Table 3. The third column in Table 3 gives the critical concentrations of the soaps calculated from eq. 9 c for those cases for which the value of m can be estimated from available data. When the value of m was not known, the CMC was calculated from eq. 9 b. Experimentally determined values for the CMC are given in the fourth column. The agreement is satisfactory. Actually the values of Table 3 do not present anything new, for they only confirm the established logarithmic relationship between CMC and the length of the hydrocarbon chain [3].

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