

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

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The values calculated for the association energy in Part I are applied to the association process that takes place in solutions of the potassium salts of α,ω -alkanedicarboxylic acids¹. The critical concentrations of these salts are calculated from the values derived for the energy of association and are compared with experimentally determined values.

In Part I it was shown that the energy of association per mole of a straight-chain monocarboxylic soap can be computed from the equation

$$\Delta G_{\text{ass}} = -620 \eta + 3\,680 \text{ cal.} \quad (10)$$

where η is the number of methylene groups in the soap molecule¹.

It should be possible to extend the same equation to the association of potassium salts of α,ω -alkanedicarboxylic acids. Obviously it is necessary to double the electrical work involved in the association process because of the presence of two charged carboxylate groups in the molecule. We then obtain

$$\Delta G_{\text{ass}} = -620 \eta + 7\,360 \text{ cal.} \quad (11)$$

where η is again the number of methylene groups in the molecule. Values for the association energies calculated from this equation for a number of alkane dicarboxylic salts are given in Table 1.

Table 1. The association energies of potassium salts of α,ω -alkanedicarboxylic acids at 20° C calculated according to eq. 11.

Salt	ΔG_{ass} cal./mole
KOOC-(CH ₂) ₈ -COOK	+2 400
KOOC-(CH ₂) ₁₁ -COOK	+ 540
KOOC-(CH ₂) ₁₄ -COOK	-1 320
KOOC-(CH ₂) ₁₆ -COOK	-2 560

Qualitatively these values are in accordance with known properties of these compounds². The potassium salt of decanedioic acid does not undergo association in aqueous solution, while in the case of the potassium salt of tridecanedioic acid, signs of association are observed only in very concentrated solutions. Association in solutions of the potassium salt of hexadecanedioic acid occurs when the concentration exceeds 0.4 molal, but the potassium salt of the octadecanedioic acid is a typical association colloid with a critical concentration of 0.05 molal².

The association energy values in Table 1 can be employed to calculate the critical concentrations of the dicarboxylic salts. The micelle formation by these salts can be treated in the same manner as in the case of normal soaps, with the difference, however, that in the application of the mass action law, two alkali ions are associated with each dicarboxylate ion. Also the number of "gegenions" bound to each dicarboxylate ion is twice the number in the case of normal soaps. In the following it is assumed that the average number of potassium ions bound is $n/m = 2 \times 0.56 = 1.12$ moles per mole salt.

We shall again choose as the starting point in our treatment the total concentration equal to three times the critical concentration. A first approximation based on eqs. 1 — 4 b in Part I¹ is that at this total concentration the concentration of unassociated paraffin-chain anions is C_{crit} and the quantity of anions bound in the micelles is $2 C_{\text{crit}}$. The total alkali ion concentration is $6 C_{\text{crit}}$, the quantity of bound cations is $2.24 C_{\text{crit}}$ and that of free cations is hence $3.76 C_{\text{crit}}$.

The free alkali ions should decrease the activity of the fatty acid ions by promoting association in accordance with expression 7. By applying successively eqs. 1 — 4 b and 7, it is found that at a total concentration $3 C_{\text{crit}}$ the activity of the free dicarboxylate ions is approximately $0.57 C_{\text{crit}}$, that of the free alkali ions is $3.28 C_{\text{crit}}$, and the concentration of the micelles is $1/m \times 2.43 C_{\text{crit}}$. By substituting these values in the expression 3 for the association energy, we find that at 20° C

$$\Delta G_{\text{ass}} = 1\,340 (2.12 - 1/m) \log C_{\text{crit}} + 1\,340/m \log (m/2.43) + 450 \text{ cal.} \quad (12)$$

According to this equation the free energy change will be largely determined by m when this has a low value. For this reason it is necessary to know the order of magnitude of m . As in the case of normal soaps, an approximate value for m can be estimated on the basis of the solubilizing power of the micelles.

Solubilization data for the potassium salts of alkanedicarboxylic acids suggest that these salts form single-layered micelles². There is reason to assume that the micellar aggregates have all three dimensions equal, as in the dilute solutions of ordinary soaps. From roentgenographic data it is known that the increase in length per methylene group in a hydrocarbon-chain is 1.25 Å and the cross-sectional area taken up by the hydrocarbon-chain in a micelle³ is about 28 Å². It hence follows that if a micelle of the potassium salt of tridecanedioic acid has equal dimensions in all directions, the micelle will contain approximately eleven dicarboxylate ions. In a corresponding manner a $\text{KOO}-(\text{CH}_2)_{14}-\text{COOK}$ micelle can be estimated to contain 17 and a $\text{KOO}-(\text{CH}_2)_{16}-\text{COOK}$ micelle 22 ions.

Table 2. The association energies of the potassium salts of α,ω -alkanedicarboxylic acids at 20° C calculated according to eq. 12.

Salt	ΔG_{ass} cal./mole
KOOC-(CH ₂) ₁₁ -COOK	2 710 log C_{crit} + 540
KOOC-(CH ₂) ₁₄ -COOK	2 750 log C_{crit} + 520
KOOC-(CH ₂) ₁₆ -COOK	2 770 log C_{crit} + 510

When these values of m are substituted in eq. 12 the values in Table 2 are obtained for the changes in the free energies in the association.

It is now possible to calculate the critical concentrations by comparing the values of ΔG_{ass} in Table 1 and Table 2. The value of C_{crit} obtained for KOOC-(CH₂)₁₁-COOK is 1.0 molal. The experimental value obtained² from a study of the solubilization of n -decanol is 1.8 molal at 40° C. The calculated and experimental values for KOOC-(CH₂)₁₄-COOK are 0.22 molal and 0.4 molal at 40° C, respectively. The agreement is satisfactory in view of the low value of the activity coefficient in the concentrated solutions involved. For KOOC-(CH₂)₁₆-COOK the calculated critical concentration is 0.075 molal and the experimental value² based on conductivity and solubilization power is 0.05 molal at 60° C.

As already pointed out, it is difficult to confirm the values derived for the free energy change. It seems, however, that the values derived for the free energy change can be used to determine whether the paraffin-chain salt undergoes association or not and to evaluate approximately the concentration where association begins.

REFERENCES

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