

The Properties and Structures of Aqueous Sodium Caprylate Solutions

VII. Activities of Caprylate Anions, and Counter Ion Binding to the Micelles

PER EK WALL and PER STENIUS

Laboratory for Surface Chemistry (Ytkemiska Laboratoriet), the Royal Swedish Academy of Engineering Sciences, Stockholm, Sweden

On the basis of the activities of the sodium ions and the mean activities for sodium caprylate the activities of the caprylate ions have been calculated. Below the c.m.c. the activity of the last mentioned ions increases linearly; in the region immediately above this concentration it passes through a maximum; above about 1.2 m the activity is almost constant but increases slightly above 2.7 m.

The activity values for the sodium and caprylate ions have been used for calculation of the counter ion binding to the micelles. There is a region with constant counter ion binding above the c.m.c. up to 1.0–1.2 m, where the counter ion binding rises to a higher level; at higher concentrations it continues to increase.

On the basis of the activities for the sodium ions and the mean activities for sodium caprylate determined in previous studies^{5,6} the activity of the caprylate ions and the counter ion binding to the micelles were calculated for round concentrations of sodium caprylate.

ACTIVITY OF CAPRYLATE IONS

The activity of the caprylate ions was calculated on the assumption that expression (1) is valid throughout the concentration range.

$$a_{C_8^-} = a_{NaC_8}^2 / a_{Na^+} \quad (1)$$

The values are given in Table 1, column 4. The curves in Fig. 1 show the dependence of the sodium and caprylate ion activities on the concentration. Below the c.m.c. the activity of the caprylate ions is slightly higher than that of sodium ions; the curve for the former rises linearly up to the c.m.c. and

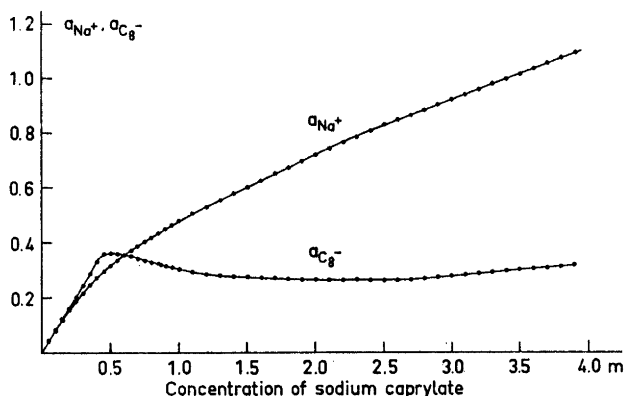


Fig. 1. The activities of the sodium and caprylate ions in sodium caprylate solutions at 20°C.

continues then to rise with a lower rate to a maximum at 0.5 m, after which it descends; between 0.6 and 1.2 m there is a decrease of about 0.07 units. Above the latter concentration the activity then changes extremely little;

Table 1. Mean sodium ion and caprylate ion activities for round sodium caprylate concentration values at 20°C.

m	a_{NaC_8}	a_{Na^+}	$a_{\text{C}_8^-}$	m	a_{NaC_8}	a_{Na^+}	$a_{\text{C}_8^-}$
0.050	0.042	0.040	0.044	1.700	0.417	0.649	0.268
0.100	0.079	0.077	0.081	1.800	0.423	0.671	0.266
0.150	0.117	0.116	0.118	1.900	0.430	0.695	0.266
0.200	0.155	0.152	0.158	2.000	0.436	0.719	0.264
0.250	0.192	0.183	0.201	2.100	0.442	0.743	0.262
0.300	0.230	0.216	0.244	2.200	0.448	0.765	0.262
0.350	0.265	0.245	0.286	2.300	0.454	0.785	0.262
0.400	0.300	0.271	0.332	2.400	0.460	0.807	0.262
0.450	0.325	0.296	0.356	2.500	0.466	0.828	0.262
0.500	0.337	0.317	0.360	2.600	0.472	0.845	0.263
0.550	0.346	0.336	0.356	2.700	0.479	0.863	0.265
0.600	0.355	0.355	0.355	2.800	0.487	0.882	0.269
0.650	0.361	0.372	0.350	2.900	0.496	0.902	0.273
0.700	0.363	0.386	0.341	3.000	0.506	0.920	0.278
0.750	0.367	0.404	0.333	3.100	0.516	0.940	0.283
0.800	0.370	0.418	0.327	3.200	0.525	0.959	0.288
0.850	0.373	0.433	0.321	3.300	0.535	0.978	0.293
0.900	0.375	0.448	0.314	3.400	0.545	0.997	0.298
0.950	0.378	0.464	0.309	3.500	0.554	1.016	0.302
1.000	0.380	0.479	0.302	3.600	0.563	1.035	0.306
1.100	0.383	0.504	0.291	3.700	0.572	1.055	0.310
1.200	0.388	0.528	0.285	3.800	0.581	1.073	0.314
1.300	0.393	0.552	0.280	3.900	0.590	1.091	0.319
1.400	0.399	0.577	0.276	4.000			
1.500	0.405	0.600	0.273				
1.600	0.411	0.623	0.271				

in fact over a large range it is practically constant. Above 2.7 there is a weak but continuous increase.

The curve for the caprylate ion activity thus has the same course, characterized of a weak maximum above the c.m.c., as was reported by Ekwall and Harva in 1943 for the activity of the laurate ions in sodium laurate solutions (on the basis of measurements with a silver/silver laurate electrode).⁷ A course of this type is predicted by theory.

It is remarkable that while the caprylate ion activity first increases and then decreases between the c.m.c. and 1.1 m, referred to as the '2nd critical concentration', it is relatively constant from the latter concentration up to about 2.7 m, the '3rd critical concentration', above which according to viscosity measurements the spherical micelles assume an anisometric form.

COUNTER ION BINDING

The experimental values for the activity of sodium ions were used for calculating the counter ion binding to the micelles. The notation was as follows:

- C_{tot} Total concentration of sodium caprylate, moles per 1000 g of water,
 $C_{\text{c}_s^-}$ Total concentration of caprylate ions that are not included in the micelles, moles per 1000 g of water,
 C_{mic} Total concentration of caprylate ions in micellar form; moles per 1000 g of water,
 α Degree of dissociation of the micellar substance,
 $a_{\text{Na}^{\text{exp}}}$ The experimental counter ion activity,
 $\gamma_{\text{Na}^{\text{exp}}}$ The experimental activity coefficient for the counter ions.

In addition, the counter ion activity is divided formally into two quantities, one referring to the ions corresponding to the free caprylate ions, and the other to those corresponding to the caprylate ions of the micelles; f' and f'' are the activity factors for the counter ions corresponding to the former and latter, respectively:

$$a_{\text{Na}^{\text{exp}}} = \gamma_{\text{Na}^{\text{exp}}} C_{\text{tot}} = f' C_{\text{c}_s^-} + f'' \alpha C_{\text{mic}} = f' C_{\text{c}_s^-} + f'' \alpha C_{\text{tot}} - f'' \alpha C_{\text{c}_s^-} \quad (2)$$

$$\gamma_{\text{Na}^{\text{exp}}} = f'' \alpha + \frac{C_{\text{c}_s^-}}{C_{\text{tot}}} (f' - f'' \alpha) \quad (2a)$$

If $f' = f'' = f$ we have

$$\gamma_{\text{Na}^{\text{exp}}} = f \alpha + \frac{C_{\text{c}_s^-}}{C_{\text{tot}}} f (1 - \alpha) \quad (2b)$$

This equation is in agreement with one derived by Bortré for the range just above the c.m.c.⁸

The curve for $\gamma_{\text{Na}^{\text{exp}}}$ versus $C_{\text{c}_s^-}/C_{\text{tot}}$ should be linear within a concentration range where $(f' - f'' \alpha)$ is constant, that is, in accordance with (2b) where α and f remain constant.

When these formulae are used it is difficult to find the correct value of $C_{C_s^-}$, the systems concentration of caprylate ions not bound to micelles. As a first approximation $C_{C_s^-}$ may be put equal to the c.m.c., and use can be made of the value of the critical concentration for micelle formation which is determined by one of the usual methods, for instance from measurements of density, viscosity, osmotic coefficient or solubilization of hydrocarbons. The curve in Fig. 2a is based on this approximation, when the c.m.c. was put equal to 0.38 m. As the curve shows, γ_{Na^+exp} versus $C_{C_s^-}/C_{tot}$ is linear over a large range above the c.m.c. The slope here ($f' - f''\alpha$) is 0.460. The extrapolation of this segment to $C_{C_s^-}/C_{tot} = 0$ gives $f''\alpha = 0.304$. From these two values we have $f' = 0.764$, and if $f' = f''$, $\alpha = 0.396$. This result indicates that the degree of dissociation of the micelles is constant over the concentration range above the c.m.c.; this is consistent with previous experience of the constant properties, constant magnitude and shape of the micelles in this region. It gives a value of 0.604 for $(1 - \alpha)$, that is, a counter ion binding of 60.4 %.

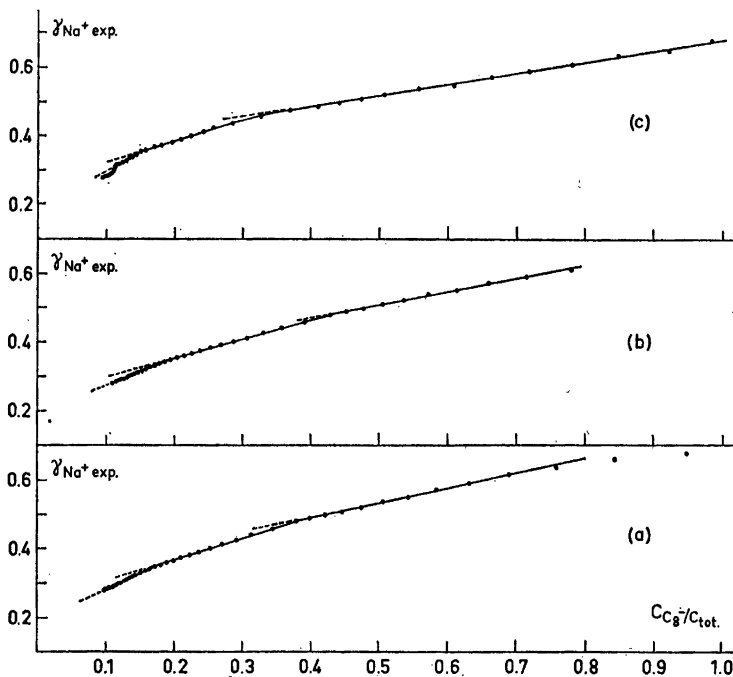


Fig. 2. Curves for γ_{Na^+exp} versus $C_{C_s^-}/C_{tot}$.

- (a) First approximation: The concentration of free caprylate ions, $C_{C_s^-}$, above the c.m.c. is assumed to be constant and equal to the value of c.m.c.
 (b) Second approximation: The value of $C_{C_s^-}$ is assumed to be constant and equal to its value at the maximum above c.m.c. The decrease in $a_{C_s^-}$ is assumed to be caused by a decrease in the activity coefficient.
 (c) Third approximation: The value of $C_{C_s^-}$ is assumed to decrease from the value 0.43 m at the maximum in the same rate as $a_{C_s^-}$.

This value is plausible and is near the 60 % determined earlier by Corrin's method⁹ for the micelles of the sodium caprylate solutions at the c.m.c.

The segment with constant slope extends to $C_{C_s^-}/C_{tot} = 0.38$, that is about up to 1.0 m. Here ends the range over which the counter ion binding is constant; at higher concentrations the curve is steeper, which means a greater binding of counter ions. Here, too, the curve is at first almost linear; it extends down to $C_{C_s^-}/C_{tot} = 0.19$. If, as above, the slope of this segment of the curve and the extrapolated value at $C_{C_s^-}/C_{tot} = 0$ are used for calculating the counter ion binding, we obtain a value of 0.730 for $(1-\alpha)$; that is, the counter ion binding has risen to 73.0 %, at which level it remains constant up to about 2 m.

Above this concentration the curve again follows a steeper course; this implies a further rise in counter ion binding; the calculation gives a binding of 82 % and above.

The first approximative evaluation of the results thus shows not only that the counter ion binding is constant in the region just above the c.m.c., and that it then rises, but also that the first rise occurs at about 1.0 m, that is to say, just below the concentration, the 2nd critical concentration, at which other methods have indicated a structural change.¹⁻⁴ A second rise occurs at about 2.0 m, that is below the concentration, the 3rd critical concentration, where the micelles begin to assume an anisometric shape.³

These calculations were based on the assumptions that $C_{C_s^-} = \text{c.m.c.} = 0.38$ m and remains constant over the whole concentration range examined; but these assumptions are not correct, for the study has shown that the activity of free caprylate ions in the region just above the c.m.c. rises slightly above the value at the c.m.c., and this means that the concentration of non-micellar caprylate is also greater; it must therefore be taken account of that the value of $C_{C_s^-}$ rises slightly above that at c.m.c. In addition it has been seen that after the maximum at 0.5 m the activity of the caprylate ions decreases again, but it is not known to what extent this is due to a reduction in the activity coefficient of the caprylate ions or in their concentration. On the assumption that the former is the case a value of 0.43 m for $C_{C_s^-}$ was calculated on the basis of our values of $a_{C_s^-}$ and a_{NaC_s} and Robinson's values for the mean activities and corresponding concentrations for non-associated sodium salts of fatty acids.¹⁰ This value was assumed to be constant above 0.5 m sodium caprylate.

This second approximation gives a curve that has the same course, with a linear segment in the region above the c.m.c. and another at higher concentrations as in the previous case (Fig. 2b), but the values obtained for α and $1-\alpha$ indicate slightly lower counter ion bindings, namely 54 % between the c.m.c. and 1.05 m, and 69 % between 1.1 and 2.4 m. Above about 2.5 m it rises to 83 %.

If, on the other hand, it is assumed that the reduction in the activity of the caprylate ions above 0.5 m is due entirely to a lowering of the concentration of free caprylate ions, from the maximum value of 0.43 m, the curve in Fig. 2c is obtained. The course of the curve is similar to that for the previous approximations. A first region with a constant counter ion binding of 50.8 % is found between 0.50 and 1.17 m, and another segment with a value of 73.4 %

between 1.17 and 2.1 m, and then an increase to about 85 %, up to about 3.2 m, with perhaps a further rise above this concentration.

The results of this test give thus — although there is some uncertainty concerning the absolute values of the counter ion binding — a full evidence for a constant level of the binding within the small micelle region from the c.m.c. up to the 2nd critical concentration, and show an increase to a higher level at the latter concentration and that the binding increases further still at higher concentrations.

These results throw also some light on the nature of the structural changes at the 2nd critical concentration. These changes are initiated by the increase in counter ion binding; as the ions apparently are bound together with their hydration water, the weight and volume of the micelles as a consequence will increase, however, without any change in their spherical shape. These changes explain the increase in viscosity observed above 1.1 m; as was shown earlier a rise in the counter ion binding to 76–77 % will be sufficient to give the observed increase in viscosity.²

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Received March 22, 1967.