

The Effect of Added NaCl on Sodium Nonanoate Micelles

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The effects of added NaCl on sodium nonanoate micelles in water have been investigated at 25 °C by several experimental techniques. The fraction of counterions associated to the micelles, β , have been measured by an ion exchange membrane electrode showing that β increases at first and then decreases as the concentration of NaCl increases beyond 0.1 molal. This result suggests a structural change in the micelles above 0.1 molal NaCl. This has been further investigated by viscosity measurements confirming the results from the measurements of β .

The partial molal volumes and compressibilities of sodiumnonanoate in NaCl-water solutions have also been measured. These quantities decrease with increasing concentration of NaCl, but do not seem to be dependent on micelle structure.

It is well known that added electrolytes affect aqueous surfactant solutions so that the CMC decreases with increasing electrolyte concentration.¹ In an earlier work² we studied the effects of added NaCl on the changes in partial molal volume and compressibility at micelle formation. The system was sodium dodecanoate (NaC_{12}) in aqueous solution and it was observed that both these thermodynamic quantities decreased with increasing NaCl concentration. Also, the fraction of counterions associated to the dodecanoate micelles increased with increasing NaCl concentration, and a linear correlation between the fraction of associated counterions and the partial molal volume change of micellization appeared.

The concentration range of NaCl in the previous investigation was 0.01–0.1 molal. Above this NaCl concentration flocculation of the sodium dodecanoate solutions occurred and no measurements could be carried out. It was, however, considered to be of interest to increase the NaCl concentration above 0.1 molal. In this work we have added NaCl

to aqueous solutions of sodium nonanoate (NaC_9). This system was chosen since it does not present any experimental difficulty like the one countered with sodium dodecanoate, and the NaCl concentration has been raised to 0.4 molal.

EXPERIMENTAL

Sodium nonanoate (NaC_9) has been made by mixing equivalent portions of nonanoic acid (R_9COOH) and NaOH. The synthesis has been described in detail elsewhere.^{3,4} The nonanoic acid was Sigma grade, >99%, and the NaOH was obtained from EKA, Sweden.

NaCl (Bakers analysed grade, 99.8%) was dried in an oven at 150 °C for 48 h. Stock solutions of 0.05, 0.1, 0.2 and 0.4 mol kg⁻¹ NaCl were made, and these solutions were used as mixed solvents. From each of these mixed solvents ten solutions of NaC_9 were made in the concentration range 0.04–0.4 mol kg⁻¹ (kg mixed solvent). All concentrations were determined by weight.

Densities were measured with a Paar density meter (DMA 02) and isentropic coefficients of compressibility were determined by ultrasound measurements. Details of the measurements have been described elsewhere.^{5,6}

The fraction of associated counterions, β , was determined by EMF-measurements, using a cation exchange membrane electrode.⁷ A capillary viscometer of the Ubbelohde type was employed to determine relative viscosities. The reproducibility of the viscosity values of the solutions was better than $\pm 0.5\%$.

The specific conductivities of all the solutions were measured and used to determine the critical micelle concentration (CMC) as a function of added NaCl.

The temperature was controlled to 25.000 ± 0.005 °C in a water bath for all the measurements.

RESULTS AND DISCUSSION

CMC as a function of added NaCl. Shinoda *et al.*¹ have demonstrated that the change in the CMC upon the addition of electrolytes can be expressed by:

$$\log \text{CMC} = -\beta \log (\text{CMC} + C_s) + \text{const}(T,P) \quad (1)$$

β is the fraction of counterions associated to the micelles, and C_s is the concentration of NaCl. The CMC for NaC₉ at different concentrations of NaCl has been determined by measurements of specific conductivities. The CMC has been determined as the break in the slope when the specific conductivities were plotted as a function of the concentration of NaC₉. The results obtained are shown in Table 1. In Fig. 1 log CMC is shown as a function of log (CMC + C_s). This plot shows good agreement between the experimental results and the linear relation proposed by eqn. (1).

From the slope of the straight line in Fig. 1, β has been determined to 0.68 ± 0.05 , which is in good agreement with previous results.⁸

β as a function of added NaCl. β has been determined by EMF-measurements using an ion exchange membrane electrode described previously.⁷ The activities of the Na⁺ ions have been determined at several concentrations above and below the CMC, and β has been evaluated according to the method of Botre *et al.*⁹ The results are shown in Table 1.

It turns out that β increases with increasing concentration of NaCl up to $C_s = 0.1$ molal, in accordance with the results for the parallel measurements with dodecanoate micelles.² However, at NaCl concentrations above 0.1 molal β decreases. A similar decrease in counterion association has been reported by Mathews *et al.*¹⁰ at the addition

Table 1. The critical micelle concentration and the fraction of associated counterions for sodium nonanoate at different concentrations of NaCl at 25 °C.

C_s	CMC ± 0.04	$\beta \pm 0.02$
0	0.210	0.64 ^a
0.05	0.204	0.71
0.10	0.188	0.76
0.20	0.160	0.68
0.40	0.115	0.64

^a Ref. 8.

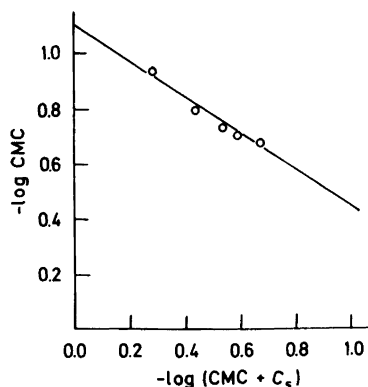


Fig. 1. Plot of log CMC for sodium nonanoate as a function of added NaCl at 25 °C according to eqn. (1).

of NaBr to CTAB-micelles (hexadecyltrimethylammonium bromide).

In pure aqueous solution the nonanoate micelles are thought to be spherical in shape.¹¹ It is also known that the addition of NaCl increases the aggregation number of the micelles.^{12,13} It seems probable that by continued addition of NaCl to this system of sodium nonanoate micelles, the aggregation number will increase beyond the limit where the nonanoate micelles can retain a spherical shape,¹⁴ and a change to rod-like or possibly lamellar micelles should occur. Such a structural change is likely to reduce the surface charge density of the micelles, and a reduction in β should result.¹⁰

Effect of added NaCl on the intrinsic viscosity of micelles. Viscosity measurements have also been carried out in order to further investigate the effect of NaCl on the nonanoate micelles. The relative viscosity of solutions, η_{rel} , can be determined from the equation:

$$\eta_{rel} = \eta/\eta_0 = td/t_0d_0 \quad (2)$$

η and η_0 are the absolute viscosities of the solution and the solvent, respectively, and t and t_0 are the corresponding viscometer flow times.

Kushner *et al.*¹⁵ have shown that the intrinsic viscosity of micelles, $[\eta]$, can be determined by the following equation:

$$(\eta_{rel} - 1)/C_m = [\eta] + AC_m \quad (3)$$

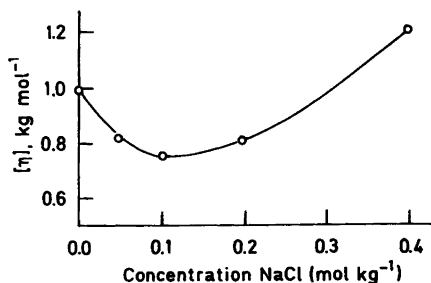


Fig. 2. Plot of the intrinsic viscosity of the sodium nonanoate micelles as a function of added NaCl at 25 °C.

C_m is the concentration of the surfactant in the micellar state, i.e. $C_m = C_{tot} - CMC$. η_{rel} is the viscosity of the micellar solution relative to the absolute viscosity of the surfactant solution at the CMC, and A is an empirical constant.

From plots of $\eta_{rel} - 1$ as a function of C_m , $[\eta]$ was determined for different concentrations of NaCl. The results are shown in Fig. 2. $[\eta]$ decreases as C_s increases up to 0.1 molal. This decrease can be explained by the reduced electroviscous effect as the charge of the micelles is reduced. However, at $C_s > 0.1$ molal the intrinsic viscosity increases. Kushner *et al.*¹⁶ have found exactly the same trend for solutions of dodecylamine hydrochloride micelles at concentrations of NaCl above 0.1 molal. They interpreted this increase in intrinsic viscosity as a result of high asymmetry of large micelles, and this interpretation was confirmed by light-scattering measurements, where a large increase in micellar weight was found.

Thus the results for the intrinsic viscosities of the nonanoate micelles confirm that a structural change of the micelles to greater aggregates takes place when $C_s > 0.1$ molal.

Effect of added NaCl on the partial molal volume. The partial molal volume for the surfactant can be determined from density measurements according to the following equation:

$$V_\phi = (d_0 - d)/md d_0 + M/d \quad (4)$$

d_0 and d are the densities of the mixed solvent and the solution, respectively. The change in partial molal volume at micelle formation, ΔV^m , can be expressed by:³

$$\Delta V^m = V_\phi^m - V_\phi^s \quad (5)$$

Acta Chem. Scand. A 33 (1979) No. 3

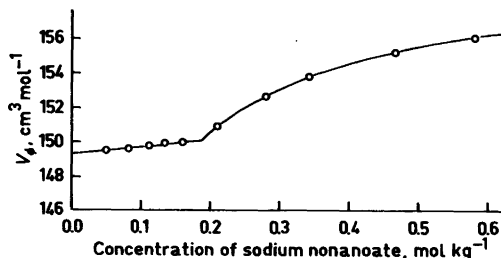


Fig. 3. Plot of V_ϕ for sodium nonanoate at 0.1 molal NaCl as a function of concentration at 25 °C.

V_ϕ^m and V_ϕ^s are the partial molal volumes of the surfactant in the micellar state and in the singly dispersed state, respectively.

Fig. 3 shows a typical plot of V_ϕ as a function of concentration sodium nonanoate. V_ϕ^s is equal to V_ϕ at the CMC, and V_ϕ^m is determined by using a saturation function to the plot above the CMC.^{3,17}

The results for V_ϕ^s , V_ϕ^m and ΔV^m at different concentrations of NaCl are shown in Table 2. Estimated uncertainty in ΔV^m is $\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$.

From Table 2 it turns out that V_ϕ^s increases linearly with C_s , and this was also found for NaC_{12} .² Musbally *et al.*¹⁸ found the same trend when urea was added to surfactant solutions.

Surfactants are known to stabilize the water structure through hydrophobic hydration of the hydrocarbon chain.¹⁹ This hydrophobic hydration gives a negative contribution to V_ϕ as the free space between the CH_2 -groups of the surfactant molecules are reduced.²⁰ Addition of electrolytes like NaCl and urea will reduce the structural hydration interactions of the hydrophobic hydration,^{18,21} and the negative contribution to V_ϕ will be reduced.

Table 2. Partial molal volumes ($\text{cm}^3 \text{ mol}^{-1}$) and the change in partial molal volume at micelle formation for sodium nonanoate in NaCl solutions at 25 °C.

C_s	$(V_\phi \pm 0.2) \text{ cm}^3 \text{ mol}^{-1}$			$(\Delta V^m \pm 0.4)$
	V_ϕ^s	V_ϕ^m	V_ϕ^m	
0	148.8	149.6	158.8	9.2 ^a
0.05	149.0	149.8	158.8	9.0
0.10	149.3	150.0	158.8	8.8
0.20	149.7	150.4	158.8	8.4
0.40	150.4	151.0	158.8	7.8

^a Ref. 8.

Thus the V_ϕ for the surfactant will increase upon the addition of NaCl, in excellent agreement with the results obtained for NaC₉. Also, the increased coulombic ion-ion interactions at the ionic head group of the surfactant when NaCl is added will tend to increase V_ϕ .

The partial molal volume of the surfactant in the micellar state, V_ϕ^m , seems remarkably constant as the NaCl concentration increases. Similar results were found for NaC₁₂ and for DTAB-micelles (dodecyltrimethylammonium bromide) in aqueous urea solutions.²¹

It is probable that the conditions in the interior of the micelles are practically independent of the size and shape of the micelles. Hence the contribution to V_ϕ^m from the true volume of the surfactant molecules and from the free space between the molecules will remain constant upon the addition of NaCl. However, at the surface of the micelles both the fraction of associated counterions and the hydrophilic hydration of the micelles change as the NaCl concentration increases. Looking closer at Table 1, it turns out that the changes in β are moderate and these changes will probably give only small contributions to V_ϕ^m . The partial molal volumes of electrolytes are known to increase as the electrolyte concentration increases,²² due to increased solute-solute interactions. The increase in volume is usually ascribed to the screening of the electrostriction of water molecules by the approach of counterions. However, at the micelle surface about 70% of the head groups of the surfactant molecules are associated to hydrated Na⁺ ions. There are two main types of interactions taking place between the micelle surface and the free ions in solution: Attraction between the free Na⁺ ions and the COO⁻ groups, and repulsion between the free and associated Na⁺ ions. The attraction between ions of opposite sign in solution gives a positive contribution to the partial molal volume, but the repulsion between ions of the same sign will give a negative contribution.¹⁹ It is possible that the constant V_ϕ^m at increased concentration of NaCl is a result of compensation between these effects at the surface of the micelles.

From Table 2 it can be seen that ΔV^m decreases linearly with increasing C_s , which was also found for NaC₁₂. In that previous work² this decrease was interpreted as a result of the increasing β , the Na⁺ ions giving a negative contribution to ΔV^m . However, from our present analysis of V_ϕ^m and V_ϕ^s it is clear that the decrease in ΔV^m must be

interpreted as a result of the reduced hydrophobic hydration and increased coulombic interactions below the CMC, giving increased values of V_ϕ^s as C_s increases. This, however, does not exclude the possibility that the associated Na⁺ ions give a negative contribution to ΔV^m .

It is important to note that the structural changes of the micelles at $C_s > 0.1$ molal cannot be detected in the volumetric quantities, and the partial molal volume of the surfactant in the micellar state seems to be independent of the structure of the micelles.

Effect of added NaCl on the partial molal compressibility. The isentropic apparent molal compressibility, $\kappa_{\phi(s)}$, can be determined from ultrasound measurements:

$$\kappa_{\phi(s)} = c^{-1}(\beta_s - \beta_{os}) + \beta_{os} V_\phi \quad (6)$$

β_{os} and β_s are the isentropic coefficients of compressibility of the mixed solvent and the solution, respectively. The change in isentropic partial molal compressibility at micelle formation, $\Delta\kappa_s^m$, can be expressed by the equation:

$$\Delta\kappa_s^m = \kappa_{\phi(s)}^m - \kappa_{\phi(s)}^s \quad (7)$$

$\kappa_{\phi(s)}^m$ and $\kappa_{\phi(s)}^s$ are the partial molal compressibilities of the surfactant in the micellar state and in the singly dispersed state, respectively. A plot of $\kappa_{\phi(s)}$ as a function of the concentration of the surfactant is similar to Fig. 3 for V_ϕ . Hence $\kappa_{\phi(s)}^s$ is determined as $\kappa_{\phi(s)}$ at the CMC, and $\kappa_{\phi(s)}^m$ is determined by a saturation function.³ Estimated uncertainty in $\Delta\kappa_s^m$ is $\pm 5 \times 10^{-4} \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$. The obtained results for κ_s^{∞} , $\kappa_{\phi(s)}^s$, $\kappa_{\phi(s)}^m$ and $\Delta\kappa_s^m$ are presented in Table 3.

Table 3. Partial molal compressibilities ($\text{cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$) and the change in partial molal compressibility at micelle formation for sodium nonanoate in NaCl solutions at 25 °C.

C_s	$(\kappa_{\phi(s)} \pm 2) \times 10^4 \text{ cm}^3 \text{ bar}^{-1} \text{ mol}^{-1}$			
	κ_s^{∞}	$\kappa_{\phi(s)}^s$	$\kappa_{\phi(s)}^m$	$(\Delta\kappa_s^m \pm 5) \times 10^4$
0	-74	-57	45	102 ^a
0.05	-72	-56	45	101
0.10	-70	-56	43	99
0.20	-66	-55	40	95
0.40	-60	-53	35	88

^a Ref. 8.

From Table 3 it is clear that the changes in the compressibilities are small when NaCl is added, and the results are similar to the sodium dodecanoate data.² $\kappa_{\phi(s)}^s$ is almost constant as C_s increases, and it seems as if the reduced hydrophobic hydration of the surfactant has very little influence on the compressibilities of the surfactant molecules.

$\kappa_{\phi(s)}^m$ decreases slightly with increasing C_s , and this can be interpreted in several ways. First, it might seem reasonable that this decrease in $\kappa_{\phi(s)}^m$ is a result of changes at the surface of the micelles. It is known that $\kappa_{\phi(s)}$ increases as the electrolyte concentration increases⁶ and thus an increase in $\kappa_{\phi(s)}^m$ might be expected when NaCl is added to the solutions. However, as mentioned above in the discussion of the volumes, compensating effects on the hydration of the micelles from attraction and repulsion at the micelle surface might explain why $\kappa_{\phi(s)}^m$ remains constant when NaCl is added.

However, it is also possible that the compressibility of the interior of the micelles decreases slightly as C_s increases. As mentioned above, the added NaCl increases the aggregation number of the micelles, and the surfactant molecules might become more closed-packed. Thus the intrinsic compressibility of the surfactant molecules might decrease when the aggregation number increases; however, further measurements are necessary to confirm the proposed explanations for the results for $\kappa_{\phi(s)}^m$.

While the decrease in ΔV^m at increasing C_s was ascribed to changes in the solutions below the CMC, it should be noticed that the similar decrease in $\Delta \kappa_s^m$ is a result of changes above the CMC. However, the structural changes of the micelles at $C_s > 0.1$ molal cannot be seen from the values of the compressibilities. Both $\Delta \kappa_s^m$ and $\kappa_{\phi(s)}^m$ seem to be linearly dependent on C_s . Thus it can be concluded that the compressibility of surfactant molecules in the micelles might be somewhat dependent on the aggregation number of the micelles, but not on the structure of the micelles.

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