Composition dependent density of ternary aqueous solutions of ionic surfactants and salts

Capturing the effect of surfactant micellization in atmospheric droplet model solutions

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Abstract
Surfactants exist in atmospheric aerosols mixed with inorganic salts and can significantly influence the formation of cloud droplets due to bulk–surface partitioning and surface tension depression. To model these processes, we need continuous parametrizations of the concentration dependent properties of aqueous surfactant–salt solutions for the full composition range from pure water to pure surfactant or salt. We have developed density functions based on the pseudo-separation method and Young’s mixing rule for apparent partial molal volumes for solutions that mimic atmospheric droplets of marine environments. The developed framework requires only model parameters from binary water–salt and water–surfactant systems and includes the effect of salinity on micellization with composition-dependent functions for the critical micelle concentration (CMC). We evaluate different models and data available in the literature to find the most suitable representations of the apparent partial molal volume of sodium chloride (NaCl) in aqueous solutions and the CMC of selected atmospheric and model surfactants in pure water and aqueous NaCl solutions. We compare model results to experimental density data, available in the literature and obtained from additional measurements, for aqueous solutions containing one of the ionic surfactants sodium octanoate, sodium decanoate, sodium dodecanoate or sodium dodecylsulfate mixed with NaCl in different relative ratios. Our model follows the experimental trends of increasing densities with increasing surfactant concentrations or increasing surfactant–salt mixing ratios both, below and above the CMC, capturing the effect of the inorganic salt on the surfactant micellization.

Keywords Atmospheric surfactants · Electrolytes · Aqueous solution density · Concentration dependent · CMC
Surfactants are organic molecules with hydrophilic and hydrophobic moieties that adsorb preferentially on interfaces. This adsorption causes a reduction of the surface tension of aqueous solutions from the value of pure water, and also causes the partitioning of surfactant molecules between the bulk and the surface compartments of solutions. Both mechanisms, i.e., surface tension depression and bulk/surface partitioning, can modify the cloud droplet formation process of atmospheric aerosols by changing the conditions of water equilibrium at the air–droplet interface (Prisle et al. 2008, 2010, 2018; Kristensen et al. 2014). The relative importance of these mechanisms on cloud formation is not easy to assess, due to the intricate dependency of droplet size and composition along the droplet growth curve. The modeling of the cloud activation process requires, in this case, the existence of continuous parametrizations of the aqueous surfactant solution properties, e.g., density and surface tension. These functions are necessary to link the conditions of water vapor–liquid equilibrium and surfactant adsorption equilibrium with mass conservation and bulk/surface partitioning. Such parametrizations are not always available as composition-dependent functions along the concentration range of atmospherically relevant multicomponent systems. Nonetheless, the thermodynamic modeling of surfactant-enriched atmospheric droplets is complex, especially because surfactants can experience self-aggregation, and this process is highly dependent on the concentration of other species, such as inorganic salts, in solution.

The aggregation process of surfactant monomers is commonly referred to as micellization and the aggregates collectively as micelles. Micellization can occur after the air–aqueous solution interface becomes saturated in adsorbed surfactant monomers and any further increase of the total surfactant concentration in solution therefore leads to accumulation and consequent self-aggregation of monomers in the solution bulk. It is a multistep process that proceeds progressively from aggregation numbers between 2 and infinity (Medoš and Bešter-Rogač 2017). However, it is typically assumed that micellization begins at a limiting surfactant concentration called critical micelle concentration (CMC), when there are observable effects of the aggregation in the properties of the solution. The formation of micelles in the bulk solution introduces discontinuities in variation of various physical properties of surfactant solutions with respect to total surfactant concentration in solution, for example in surface tension, electrical conductance, specific heat, osmotic pressure, and electromotive force (Misra and Somasundaran 2008). Often, these properties reach a minimum value at the CMC, or the rate of change with respect to further increase in concentration of dissolved surfactant in solution changes discontinuously. Above CMC, surfactant monomers coexist with micelles, which can assume a wide range of structures. Each micelle constitutes a microscopic pseudo-phase with specific properties in terms of size, geometry, aggregation number, and concentration number in solution (Santos et al. 2016). This causes departures from ideal solution behaviour, with stronger composition dependencies than those captured by conventional thermodynamic frameworks based on activity coefficients, such as E–AIM (Clegg et al. 2001, 2003) and AIOMFAC (Zuend et al. 2008, 2012, 2013).

Recently, Malila and Prisle (2018) presented the monolayer model, a semi-empirical framework that combines composition-dependent densities, with an equilibrium surface tension model, to capture droplet nonidealities during calculations of cloud droplet formation with bulk/surface partitioning. In the monolayer model, all the species distribute between the droplet bulk and the droplet surface according to their surface activity and molecular volume. The model relies on composition-dependent density functions to correlate the mass and volume of the droplet compartments. Composition-dependent surface
tension parametrizations are also needed to resolve the adsorption isotherm. The use of composition-dependent functions represents a simpler and experimentally more feasible way to overcome limitations imposed by the lack or scarcity of activity coefficient data or models for surface-active species. The monolayer model has been successfully implemented to predict the activation point of submicron aerosols comprised of both pure and mixture of surfactants with inorganic salts (Lin et al. 2018, 2020).

Here, we introduce a framework to build continuous parametrizations for the liquid density of aqueous solutions containing an ionic surfactant and an inorganic salt. Our model is based on the pseudo-phase separation method (Shinoda and Hutchinson 1962) and the concept of apparent partial molal volume of aqueous electrolyte solutions (Young and Smith 1954). This framework requires experimental data only for binary water–surfactant and water–salt systems and can therefore be flexibly applied to describe a wide range of higher-order mixtures. It can be implemented to calculate the density of solutions along the full composition range from pure water to pure salt or pure surfactant. It also includes the effect of salinity on the onset of micellization by means of composition-dependent functions for the critical micelle concentration, the variation of the surfactant partial molal volume during micelle formation, and the degree of counterion binding. Although our model was specifically built for calculating cloud droplet activation of surfactant-enriched aerosols, it has applications in the pharmaceutical, cosmetic and food industries, where sodium fatty acid salts are used as foamy agents (Kristen-Hochrein et al. 2011), additives (Kabir-ud et al. 2015), and pharmaceutical vehicles (Maher et al. 2009; Gupta et al. 2018).

In this work, we demonstrate the performance of our density model for ternary systems comprising water, sodium chloride and one of the ionic surfactants; sodium octanoate (NaOct), sodium decanoate (NaDec), sodium dodecanoate (NaDod) or sodium dodecylsulfate (NaDS). These compounds have been found in atmospheric aerosols from marine sources (Sicre et al. 1990; Mochida et al. 2002; Cochran et al. 2017; Shaharom et al. 2018; Cravigan et al. 2019). They have also been found in aerosol samples collected in high mountain, rural and urban areas, likely released as airborne particles from decaying plant leaves or as particulate matter in biomass burning emissions (Ren et al. 2016). We compare the model results to experimental density measurements of aqueous solutions with different surfactant–salt mass mixing ratios at surfactant concentrations up to the respective CMCs.

2 Model description

Aqueous surfactant–salt solutions are represented as ternary systems, where water, the ionic surfactant (MX) and the inorganic salt (MY) are labeled as components 1, 2 and 3, respectively. This framework specifically describes solutions, where the surfactant and the inorganic salt share the surfactant counterion (M$^+$/M$^-$) as a common ion. The formulation can be used as presented either for a cationic (X$^+$) or anionic (X$^-$) surfactant. It may also be extended to other types of inorganic salts, which will then require the adjustment of the micellization reaction parameters based on experimental data to account for the ion specificity during ion pairing, counterion binding and degree of hydration in the presence of multiple counterions in solution (Collins 1997; Kunz 2009).

Solution concentration is here expressed in units of molality, where each solution contains $m_2$ moles of surfactant per kilogram (kg) of pure water, $m_3$ moles of the inorganic salt per kg of pure water, as well as $m_1 = s = 55.56$ moles of water in 1 kg of pure water (component 1, the solvent). We assume complete dissociation of the strong electrolytes in aqueous solution. Dissociation factors are equal to 2 for both organic and inorganic salts.
After dissociation, at concentrations below CMC, the solution contains surfactant anions $X^-$, coions $Y^-$, and counterions $M^+$ from $MY$ and $MX$.

When the surfactant concentration in solution reaches the CMC, surfactant ions and counterions form aggregates, or micelles, that coexist in solution as

$$nX^- + qM^+ \xrightleftharpoons{K} (M_qX_n)^{(q-n)},$$

(1)

where $(M_qX_n)^{(q-n)}$ represents the micelle, $n$ is the aggregation number or number of surfactant ions per micelle, $q$ is the number of counterions bound to each micelle and $K$ is the equilibrium constant for the micellization reaction. Both $q$ and $n$ are related to the degree of the counterion binding $\beta$ as $q=n\beta$. When the surfactant concentration $m_2$ exceeds the CMC, the surfactant ions in solution co-exist in equilibrium between the monomeric and micellar states.

Although micellization occurs in a multistage process with aggregation numbers that increase with increasing surfactant concentrations, the process is often simplistically modeled as a single equilibrium reaction with an average aggregation number (Medoš and Bešter-Rogač 2017). Aggregation numbers can vary from ten to several hundreds of molecules depending on the chemical nature and concentration of the surfactant, the solution ionic strength, the presence of other surfactants and the temperature (Mazer et al. 1976; Hayashi and Ikeda 1980; Bales et al. 1998). We build our framework using equivalent concentrations in molecular form for all species to simplify the representation. Below CMC, dissolved surfactant monomers in the solution bulk are in equilibrium with monomers adsorbed at the air–solution interface. When surfactant monomers are ionic, a fraction of the counterions are preferentially adsorbed at the solution interface together with the surfactant ions, whereas the remaining counterions and coions from the added inorganic salt remain in the bulk solution (Kralchevsky et al. 1999; Johnson and Tyrode 2005).

We first assume that we can use the apparent partial molal volume $\phi_i$ of the species $i$, instead of the partial molar volume $\bar{\phi}_i$, as a measure of the contribution of species to the total volume of the solution. The total volume of the solution comprising 1 kg of water and $m_i$ moles per kg of water for each species $i$ can then be calculated as the addition of the individual contributions of the species in proportion to their molal concentrations as

$$V_T = \sum_{i=1}^{3} n_i \bar{V}_i = sV_1^\circ + \sum_{i=2}^{3} m_i\phi_i = s\frac{M_1}{\rho_1} + \sum_{i=2}^{3} m_i\phi_i,$$

(2)

where $V_T$ is the total volume of the solution in m$^3$, $V_1^\circ$ is the molar volume of pure water in cm$^3$ mol$^{-1}$, $\rho_1^\circ$ is the density of pure water in kg m$^{-3}$, $M_1$ is the molecular weight of water in kg mol$^{-1}$, and $m_i$ is the molality of species $i$ in the solution in mol kg$^{-1}$. The solvent (component 1) has a molality equivalent to $m_1 \equiv s = 55.56$ moles per kg of water.

We then assume that each solvent molecule occupies the same volume in solution as in its pure form, and all departures from the ideal solution behaviour caused by solvent–solute and solute–solute interactions are considered via $\phi_i$, while the contribution of the solvent to the total volume of the solution is unaltered (Millero 1971). The apparent molal volume is a concept formulated to capture the nonidealities in aqueous electrolyte solutions. Its descriptive function follows the Debye–Hückel theory as

$$\phi_i = \phi_i^\infty + A_v m_i^1 + B_v m_i^2 + C_v m_i^3 + \ldots,$$

(3)

where $\phi_i^\infty$ is the apparent molal volume of species $i$ at infinite dilution, $A_v$ is the Debye–Hückel constant in volume units, and $B_v$ and $C_v$ are model parameters (Millero 1971). The first term accounts for the nonidealities caused by long-range electrostatic forces between
ionic species, while the second and third terms represent the non-electrostatic solute–solute binary and ternary interactions. Values of $A_v$ are 1.840914 and 1.874328 in cm$^3$ kg$^{0.5}$ mol$^{-1.5}$ at 296.15 K and 298.15 K, respectively (Millero 2014).

Values for the model parameters $B_v$ and $C_v$ are found by fitting data of the apparent partial molal volume $\phi_i$ in solutions of variable concentration. The $\phi_i$ values are experimentally determined as the ratio between the difference in the volume of solution and the volume of solvent before mixing and the number of moles of species $i$ added (Millero 1971). Typically, $\phi_i$ is estimated for binary systems (water–solute) since its determination in multicomponent systems with higher degrees of freedom is difficult due to the restrictions that must be simultaneously imposed on other substances.

For ternary water–surfactant–salt solutions, the density can be calculated with a pseudo-binary approach that uses the mean apparent molal volume $\bar{\phi}$ of the solutes from the mixing rule of Young and Smith (1954) as

$$\bar{\phi} = \frac{m_2\phi_2 + m_3\phi_3}{m_2 + m_3}, \quad (4)$$

where $\phi_2$ and $\phi_3$ are estimated using data for each of the binary systems, water–surfactant and water–salt, both at a molality equal to $m_2 + m_3$. This mixing rule has been widely used to estimate partial molar volumes of electrolytes in multielectrolyte solutions (Humfrey 1987; Millero 2014). To the best of our knowledge, this mixing rule has not been implemented yet to describe surfactant systems mixed with inorganic salts.

Once $\bar{\phi}$ is known, we can derive the density of the solution from the definition of mean apparent volume (Millero 1971) as

$$\phi = \frac{V}{m_2 + m_3} = \frac{V^T - sV_1^o}{m_2 + m_3}. \quad (5)$$

Combining Eq. 5 with the formal definition of density, we obtain the expression to calculate the density of the solution as function of the molality of the surfactant and the inorganic salt in solution as

$$\rho = \frac{1 + m_2.\bar{m}_2 + m_3.\bar{m}_3}{\frac{1}{\rho_1} + 1 \times 10^{-6}\bar{\phi} (m_2 + m_3)}, \quad (6)$$

where $\bar{m}_2$ and $\bar{m}_3$ represent the molecular weight of the surfactant and the salt, the numerator $1 + m_2.\bar{m}_2 + m_3.\bar{m}_3$ is the total mass of the solution and the denominator is the total volume of the solution as defined in Eq. 2. The scaling factor $1 \times 10^{-6}$ guarantees consistent units to have densities expressed in kg m$^{-3}$ and $\bar{\phi}$ in cm$^3$ mol$^{-1}$. Finally, we need to include the changes to $\phi_2$ induced by micellization at the given salinity level of the solution.

### 2.1 Micellization

At surfactant concentrations above the CMC, micellization reduces the total molality of solute species from the stoichiometric value of $2m_2 + 2m_3$ and correspondingly changes the apparent partial molal volume of the surfactant. The solution contains surfactant molecules both in monomeric form and in micellar form. Each surfactant molecule (or ion in the case of an ionic surfactant) occupies a fixed volume equal to $\phi_{2,CMC}$. The number of surfactant molecules in monomer form is restricted by the CMC. All the excess surfactant molecules are accounted for in the micellar pseudo-phase, where each one occupies a volume equal to $V_{Mic}$. The value for $V_{Mic}$ is estimated from experimental measurements of the change in solution molar volume $\Delta V_{Mic}$ at the onset of micellization, as $V_{Mic} = \Delta V_{Mic} + \phi_{2,CMC}$.
The pseudo-phase separation method does not need explicit consideration of the number of aggregation or shape of the surfactant aggregates.

The ratio between the number of molecules in micellar form and the total number of surfactant molecules is estimated using the degree of micellization $\xi$ defined as (DeLisi et al. 1980)

$$\xi = H (m_2 - \text{CMC}) \left( \frac{m_2 - \text{CMC}}{m_2} \right),$$

where $H (x)$ is the Heaviside function. The value of $\xi$ experiences a step change at the CMC moving progressively from zero to positive numbers with increasing surfactant concentrations. Solution, where $m_2 > \text{CMC}$, then contains surfactant in monomeric form at a concentration equal to $(1 - \xi) m_2$ and micelles at concentration equal to $\xi m_2 n^{-1}$. When $m_2 < \text{CMC}$, the monomeric forms of the surfactant show an apparent partial molal volume $\phi_2$ that depends on surfactant concentration. When $m_2 \geq \text{CMC}$, the solution is saturated with respect to surfactant and the apparent partial molal volume of the monomeric form reaches a maximum value equal to $\phi_2 \text{CMC}$, whereas the micellar pseudo-phase occupies a molar volume equal to $V_{\text{Mic}}$. A general expression for the apparent molal volume of the surfactant $\phi_2$ can be written in terms of the Heaviside step function $H$ as

$$\phi_2 = H (\text{CMC} - m_2) \left( \phi_2^\infty + A_v \sqrt{m_2} + B_v m_2 \right) + H (m_2 - \text{CMC}) \left( \xi \phi_2 \text{CMC} + (1 - \xi) V_{\text{Mic}} \right)$$

Our basic assumptions stem from the pseudo-phase separation method as follows: (i) all micelles behave equally and have the same thermodynamic and volumetric properties, (ii) all micelles behave as in a liquid state and form solutions for which partial molar volumes are similar to molal volumes, and (iii) the activity of micelle-forming compounds remains constant above the CMC (Shinoda and Hutchinson 1962). Micelles can be treated as a separate pseudo-phase, even when their dimensions are very small compared to those normally characteristic in macroscopic phases”, and even when they do not lead to an effectively infinite aggregation number as corresponding to a true phase separation (Shinoda and Hutchinson 1962). As micelles are capable of acting as both sink and source of surfactant molecules in solution, mimicking phase-like behaviour, they can be treated as a thermodynamic phase, even when in a strict sense they clearly are not one (Holland and Rubingh 1992).

For sodium n–alkycarboxylate surfactants such as sodium octanoate, sodium decanoate and sodium dodecanoate, micellization does not occur as a single-stage process. Surfactant aggregation rates increase progressively with increasing concentrations, and the entire process is more adequately represented by a two-stage micellization with formation of small aggregates with 3 to 10 surfactant molecules in the earlier stage, and formation of larger aggregates with 11 to 30 surfactant molecules in the later stage (Medoš and Bešter-Rogač 2017).

To keep consistency with the pseudo-phase separation method, micellization is modelled as a step-change process occurring at CMC, after which all excess surfactant molecules occupy an apparent molal volume equal to $\phi_2 \text{CMC}$. The underlying assumption is that micellization occurs with an aggregation number $n \to \infty$, while the ratio of the activity coefficients remains constant above CMC in a measured concentration range (Perger and Bešter-Rogač 2007; Burchfield and Woolley 1984). This allows us to use a framework that can be added to calculations of cloud droplet activation without significant increases in the computing times.

The surfactant CMC is the key property in our framework. We have tested the most prominent models for predicting CMC available in the literature against experimental CMC values for binary water–surfactant systems. Results are reported in the supporting information. The CMC values used in our calculations are reported in Table 1.
| Property               | NaOct                  | NaDec                  | NaDod                  | NaDS                  |
|------------------------|------------------------|------------------------|------------------------|------------------------|
| Formula                | CH$_3$(CH$_2$)$_6$COONa| CH$_3$(CH$_2$)$_8$COONa| CH$_3$(CH$_2$)$_{10}$COONa| CH$_3$(CH$_2$)$_{10}$CH$_2$SO$_4$Na |
| $M_2$ [g mol$^{-1}$]   | 166.194                | 194.247                | 222.034                | 288.380                |
| $T_{Kraft}$ [K]        | $<$273.15$^a$          | 286.14$^a$             | 291.45$^a$             | 286.53$^d$             |
| CMC$^{bin}$ at 296.15 K [mol kg$^{-1}$]$^a$ | 0.3870                | 0.1163                 | 0.0277                 | 0.008292$^b,c$         |
| CMC$^{bin}$ at 298.15 K [mol kg$^{-1}$]$^a$ | 0.3829                | 0.1136                 | 0.0272                 | 0.008282$^b,c$         |
| Surface tension at CMC @ 296.15 K [mN m$^{-1}$] | $^{24c}$               | $^{27c}$               | $^{22c}$               | $^{39f}$               |

a: Blanco et al. (2005); b: Hossain et al. (2014); c: Mukerjee and Mysels (1971); d: Vautier-Giongo and Bales (2003); e: Prisle et al. (2010); f: @295.15 K Persson et al. (2003)
2.2 Effect of salts on micellization

When a strong electrolyte, such as sodium chloride, is added to an aqueous surfactant solution, the partial molal volume, as well as the rest of surfactant thermodynamic properties (activity, partial molar enthalpy), may change significantly due to ion–ion interactions between the surfactant’s monomer forms \((X^-)\) and ions from the added salt. The inorganic salt also modifies the equilibrium position of the micellization process. We must therefore carefully distinguish between the micellization parameters observed in binary water–surfactant solutions \((\text{CMC}^{\text{bin}}, \Delta V^{\text{bin}}_{\text{mic}}, \Delta H^{\text{bin}}_{\text{mic}}, n^{\text{bin}}, \beta^{\text{bin}})\) and those observed in the ternary water–surfactant–salt solutions \((\text{CMC}^{\text{ter}}, \Delta V^{\text{ter}}_{\text{mic}}, \Delta H^{\text{ter}}_{\text{mic}}, n^{\text{ter}}, \beta^{\text{ter}})\). In general, increasing the electrolyte content in solution leads to increasing counterion binding, but the magnitude and direction of the changes depend on the individual properties of interacting ions and also on those of the polyion (surfactant ion-surfactant counterion-inorganic salt ion) formed at the micellar surface (Vlachy et al. 2008).

If the difference between the absolute heats of hydration of the ions \(M^+\) and \(X^-\) is close to zero, the two ions will form a contact ion pair expelling the hydration spheres between them (Kunz 2009), regardless of the degree of hydration of the individual ions as explained by the law of matching water affinities (LMWA) (Collins 1997). The tendency of alkylcarboxylate surfactants to form ion pairs decreases along the series \(\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+\) (Moreira and Firoozabadi 2010). The close proximity between \(M^+\) and \(X^-\) ions also causes a more effective screening of the micelle surface electrical charge and decrease in the head surface area (Vlachy et al. 2008; Kunz 2009; Salis and Ninham 2014). With a more compact surface structure, the degree of micelle counterion binding changes and the aggregation number decreases along the same series \(\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+\) while the \(\text{CMC}^{\text{ter}}\) of the surfactant changes in the opposite direction as \(\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+\). In the case of alkylsulfate surfactants, these trends reverse their order because the difference in hydration enthalpies with respect to the sulfate headgroup changes. For example, the tendency to form ion pairs increases as \(\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+\). Moreira and Firoozabadi (2010), Kim et al. (2001), Johnson and Tyrode (2005), and Weißenborn and Braunschweig (2019)

To predict the effects on micellization caused by increasing \(M–X\) ionic interactions requires a robust thermodynamic framework and reliable experimental data, which are often not available for systems of atmospheric relevance. We here consider effects on micellization via two different mechanisms, first through the change in surfactant \(\text{CMC}^{\text{ter}}\) and second through the change in \(\Delta V_{\text{Mic}}^{\text{ter}}\) during micellization.

We demonstrate the application of our model for selected systems comprising ionic sodium \(n\)-alkylcarboxylate surfactants or sodium dodecylsulfate mixed with sodium chloride. In all the cases we expect that \(M–X\) interactions will lead to formation of direct contact ion pairs at the micellar surface, causing a reduction of the partial molal volume of the surfactant during micellization \(\Delta V_{\text{Mic}}^{\text{ter}}\) and an increase in the degree of counterion binding, as it was observed in \(\text{NaDod–NaCl}\) solutions by Høiland and Vikingstad (1978).

Experimental data for the change in partial molal volume of the surfactant upon formation of micelles in mixed electrolyte solutions are scarce. We fitted the \(\Delta V_{\text{Mic}}^{\text{ter}}–m_{\text{NaCl}}\) data presented by Høiland and Vikingstad (1978) for \(\text{NaDod–NaCl}\) solutions at 298.15 K and found that \(\Delta V_{\text{Mic}}^{\text{ter}}\) decreases linearly with increasing \(m_{\text{NaCl}}\) as

\[
\Delta V_{\text{Mic}}^{\text{ter}} = \Delta V_{\text{Mic}}^{\text{bin}} - 23.35\ m_3 + 4.681\ \beta_{\text{ter}},
\]

(9)
where $\Delta V_{\text{Mic}}^\text{ter}$ and $\Delta V_{\text{Mic}}^\text{bin}$ are in units of cm$^3$ mol$^{-1}$ and represent the change in partial molal volume of the surfactant during micellization in the ternary surfactant–salt system and in the binary water–surfactant system, respectively. For NaOct–NaCl or NaDec–NaCl systems, we assume the same equation for the $\Delta V_{\text{Mic}}^\text{ter}$ values with increasing $m_3$. Mean values for $\Delta V_{\text{Mic}}^\text{bin}$ at 298.15 K are 8.75, 9.55 and 11.0 cm$^3$ mol$^{-1}$, and values for $\beta^\text{bin}$ at 298.15 K are 0.60, 0.68 and 0.74 for binary aqueous NaOct, NaDec, and NaDod, respectively (Vikingstad et al. 1978).

We fitted the $\beta^\text{ter} - m_{\text{NaCl}}$ variation to the experimental data for NaDod–NaCl solutions at 298.15 K reported by Vikingstad et al. (1978) and found that $\beta^\text{ter}$ increases linearly with the salt concentration $m_3$ as

$$\beta^\text{ter} = \beta^\text{bin} + 2.23 m_3,$$

where $\beta^\text{bin}$ is the degree of counterion binding in the binary water–surfactant system. Due to lack of experimental data for the NaOct–NaCl and NaDec–NaCl systems, we assume a similar dependence of $m_3$ between $\beta^\text{ter}$ and $\beta^\text{bin}$ for NaOct–NaCl and NaDec–NaCl systems, as was found for the NaDod–NaCl system.

The addition of inorganic salts to aqueous surfactant solutions often causes a reduction in CMC$^\text{ter}$ from the value of CMC$^\text{bin}$, which can be represented by the empirical Corrin–Harkins equation (Corrin and Harkins 1947). This commonly used approach has an important drawback in the assumption of a unique proportionality constant between the CMC$^\text{ter}$ and $m_3$, which does not capture the expected ion specific effects (Karakashev and Smoukov 2017). We therefore use the correction of the Corrin–Harkins equation by Karakashev and Smoukov (2017) as

$$\ln \text{CMC}^\text{ter} = \ln \text{CMC}^\text{bin} - \frac{K_g}{1 + K_g} \ln \left(1 + \frac{M_3}{\text{CMC}^\text{ter}}\right),$$

where $M_3$ is the salt molarity in solution and CMC$^\text{bin}$ represents the intrinsic value of the critical micelle concentration in the absence of added salt.

The parameter $K_g$ is the equilibrium adsorption constant of the anionic surfactant calculated as

$$K_g = 0.24\eta + 0.2669 + 0.22H (N - 17) \quad \text{for} \quad 0.1 \leq \eta \leq 1.3,$$

and

$$K_g = 0.0026\eta + 0.6075 + 0.22H (N - 17) \quad \text{for} \quad 0.13 \leq \eta \leq 1,$$

where $N$ is the number of the carbon atoms into the surfactant’s hydrocarbon tail (e.g., for sodium dodecanoate the surfactant’s head is the group -COO$^-$ and $N_{\text{Dod}} = 11$) and $H$ is again the Heaviside step function. The salt-saturation multiplier $\eta$ is calculated as

$$\eta = -\frac{M_3}{\text{CMC}^\text{bin}} \left(\frac{u_o}{k_BT}\right),$$

where $M_3$ is the salt concentration in units consistent with those used for CMC$^\text{bin}$ in Eq. 11, $u_o$ is the specific adsorption energy at the air–water interface of the counterion of the added salt, in our case sodium ions. The term $u_o/(k_BT) = -0.33$ represents the dimensionless form of the same variable referred to the solution thermal energy (Karakashev and Smoukov 2017). The CMC$^\text{ter}$ at a given salt concentration is found numerically from Eq. 11.

CMC$^\text{ter}$ decreases with increasing salt concentration as shown in the supporting information where we compare experimental CMC$^\text{ter}$ values to model results using Eq. 11 for NaDec–NaCl aqueous solutions at 296.15 K in Fig. S5 and NaDS–NaCl solutions at 298.15 K in Fig. S6.
Increasing the electrolyte content in the solution lead to lower values for the surfactant area and higher aggregation numbers (Mazer et al. 1976; Hayashi and Ikeda 1980). In the phase-separation method, micellization occurs in a step-function at CMC, after which all excess surfactant molecules occupy an apparent molal volume equal to $\phi_{\text{CMC}}^2$. The variation of the structure and number of surfactant monomers in the aggregates with increasing inorganic salt concentration is not explicitly accounted for. These salt-induced changes are implicitly included in the change in the surfactant partial molal volume of micellization Eq. 9 and the degree of counterion binding Eq. 10, as well as in the CMC$^{\text{ter}}$ Eq. 11, Eq. (S5) or Eq. (S6).

2.3 Apparent partial molal volume of the salt

We consider three different approaches to estimate the apparent molal volume of sodium chloride $\phi_3$: (i) the semi-empirical model of Rogers and Pitzer (1982) based on Pitzer–Debye–Hückel theory, (ii) the modified version of the former by Archer (1992) and (iii) the empirical fitting of experimental data presented by Rowe and Chou (1970). The performance of each model to represent the behaviour of $\phi_3$ is assessed using the absolute errors calculated with predicted and experimental values of the density of aqueous solutions of NaCl in a temperature range from 273.15 K to 373.15 K at a pressure equal to 1 atm reported in the literature (Pitzer et al. 1984). Results of the assessment are shown in Fig. S7 of the supporting information. Our modified version of the model by Rogers and Pitzer (1982) yields the lowest absolute error values and higher stability for temperatures in the range of typical atmospheric conditions and was therefore used to represent the apparent partial molal volume $\phi_3$ of NaCl in the results presented below.

The apparent partial molal volume of NaCl $\phi_3$ in the solution (in units of cm$^3$mol$^{-1}$) according to the model by Rogers and Pitzer (1982) is calculated as

$$\phi_3 = \phi_3^\infty + 2A_v \frac{\log \left(1 + b\sqrt{T}\right)}{2b} + 2RT \left(m_3 B_3^v + m_3^2 C_3^v \right),$$  

where $b$ is a model parameter equal to 1.2 kg$^{0.5}$ mol$^{-0.5}$ equal for all electrolyte systems and $I$ is the ionic strength of the solution defined as $I = 0.5 \sum z_i^2 m_i$, where $z_i$ is the ion valence.

In its original formulation, the model parameters $\phi_3^\infty$, $B_3^v$, $C_3^v$ had to be resolved from highly nonlinear equations of up to 28 constants with temperature and pressure dependence. Using this formulation, the model can be used at temperatures from 273.15 K to 573.15 K and pressures from 1 bar to 1000 bar. We simplify these expressions to work in the range of atmospheric conditions at temperatures between 273.15 K and 373.15 K and pressure equal to 1 bar. Our modified temperature-dependent equations for $\phi_3^\infty$, $B_3^v$, $C_3^v$ were obtained by fitting the experimental densities for NaCl solutions presented by Pitzer et al. (1984). The model parameters $\phi_3^\infty$, $B_3^v$, $C_3^v$ can be calculated as

$$\phi_3^\infty = -0.001462T^2 + 0.9609T - 139.9 \quad (15a)$$

$$B_3^v = 0.2694 \exp\left(-0.03379T\right) + 2.611 \times 10^{-8} \exp\left(0.01245T\right) \quad (15b)$$

and

$$C_3^v = -0.04196 \exp\left(-0.03719T\right) \quad (15c)$$

where $T$ is the temperature in kelvin, $\phi_3^\infty$ is the apparent partial molal volume of NaCl in a hypothetical infinitely dilute solution in units of (cm$^3$ mol$^{-1}$), $B_3^v$ is in units of kg mol$^{-1}$ and $C_3^v$ is in units of bar kg$^2$ mol$^{-2}$.
3 Experimental methods

We measured densities for ternary aqueous surfactant solutions comprising sodium chloride and one of the surfactant salts sodium octanoate (NaOct), sodium decanoate (NaDec) and sodium dodecanoate (NaDod).

Aqueous solutions were prepared with de-ionized water (18.2 MΩ-cm resistivity from a Milli-Q Plus Ultra Pure Water System), NaOct (Sigma, capillary GC, minimum 99%), NaDec (Fluka, purum 98%), NaDod (Sigma, Sigma Grade 99–100%) and NaCl (Riedel-de Haën, >99.8%). Chemicals were dried overnight at < 80°C to evaporate any volatile impurities and used without further purification. Thermal degradation of these fatty acid sodium salts occur at higher temperatures, < 190°C, as it was discussed in section 5 of the supporting information.

Stock solutions were prepared in 250 mL flasks by weighing the required amounts of chemicals and water directly into the flask placed on a precision scale (Precisa junior 310M, Precisa Gravimetrics AG, Switzerland). For each surfactant–salt mixing ratio, a stock solution was prepared and successively diluted to obtain samples of different concentration along a dilution series. At each concentration, the sample was extracted from this stock solution, after which the remaining amount of the solution was diluted to the next concentration. At each sample extraction and further addition of water, the amount was carefully monitored and the new concentration along the dilution series was calculated. The first sample with highest concentration was extracted at the initial composition from the stock solution. During sample preparation, a few of the aqueous stock solutions were heated up to 30–35 °C for a period of a few (< 5) minutes to reduce the amount of time to fully dissolve all solute. The first sample was not extracted until the solution was believed to be cooled to room temperature.

For each solution concentration, the density was measured by weighing a precisely defined volume of the sample as contained within one of two alternating pyknometers (10 mL and 50 mL) on the same precision scale as was used for preparing the stock solution. Laboratory temperatures were kept constant at 296.15 K–297.15 K by a thermostat air-conditioning system. Uncertainties for the experimental density measurements are estimated between 0.03 kg m⁻³ and 0.15 kg m⁻³ as reported in the supporting information. We measured the concentration dependent densities of aqueous solutions containing NaOct, NaDec or NaDod mixed with NaCl at surfactant/salt mass ratios of 100/0, 80/20, 50/50 and 20/80. The complete set of measured density values at 296.15 K as a function of concentration are also reported in Tables S2–S4 of the supporting information. For NaDS–NaCl solutions, we have used the experimental values reported by Kushner et al. (1952) for comparison to our density model framework.

4 Results and discussion

4.1 Binary surfactant solutions

The expressions for temperature-dependent functions of model parameters $\phi_1^\infty$, $\phi_2, \text{CMC}$, $B_v$ and $\Delta V_{\text{mic}}^{\text{bin}}$ for the aqueous surfactant solutions in question are shown in Table 2, together with the temperature range $T_{\text{range}}$, at which correlations can be used. These expressions were obtained by fitting experimental data reported in the literature as previously described in Table 2.
### Table 2: Parametrizations for binary surfactant solutions

| Surfactant | $\phi_2^{\infty}$, $\phi_{2,\text{CMC}}$, $B_v$, $\Delta V_{\text{mic}}^{\text{bin}}$ | $N$ | $T_{\text{range}}$ (K) |
|------------|-------------------------------------------------|-----|-------------------------|
| NaOct$^a$  | $0.19T + 76.47$ | 5   | 288.15–308.15           |
|            | $0.234T + 64.49$ |    | $0.5875T - 174.6$      |
|            | $T - 282.2$    |    | $-0.07T + 35.03$       |
| NaDec$^a$  | $0.2762T + 82.06$ | 10  | 283.15–328.15          |
|            | $0.3004T + 75.65$ |    | $0.002785T^2 - 1.648T + 244.5$ |
|            |                  |    | $-0.1107T + 44.5$      |
| NaDod$^a$  | $0.3053T + 106.4$ | 8   | 293.15–328.15          |
|            | $0.3053T + 106.4$ |    | $-35.26 \exp \left(- \frac{T - 317.3}{7.893} \right)^2 + 90.18 \exp \left(- \frac{T - 301.6}{47.41} \right)^2$ |
|            | $-0.08864T + 39$ |    |                        |
| NaDS$^b$   | $0.44T + 97.55$ | 5   | 293.15–318.15          |
|            |                  |    | $0.1213T^2 - 74.28T + 1.142 \times 10^4$ |
|            | $12^c$           |    |                         |

---

$a$: Blanco et al. (2005); $b$: Hossain et al. (2014); $c$: Franks et al. (1968) at 298.15 K
The presented temperature-dependent functions for surfactant apparent molal volume at the CMC, $\phi_{2,\text{CMC}}$, and the surfactant apparent molal volume at infinite dilution, $\phi_{2}^{\infty}$, show increasing tendencies with increasing temperature, as is expected for hydrophobic solutes in water (DeLisi et al. 1980). The opposite tendency is observed for the apparent molal volume upon micellization, $\Delta v_{\text{mic}}^{\text{bin}}$, due to increase in the volume occupied by a surfactant molecule in the micellar state after aggregation (Blanco et al. 2005). With the exception of NaOct solutions, the parameter $B_v$ is always positive, indicating positive deviation from Debye–Hückel theory, which is likely due to ion–ion interactions or ion solvation effects at higher concentrations. The values of $B_v$ also show a positive parabolic behaviour with increasing temperature, which reflects the competition between the solute–solute attractive forces and the thermal molecular motion that disrupts aggregation. Again, an exception to this parabolic tendency was observed for NaOct solutions with negative $B_v$ values at temperatures below 298.15 K. This behaviour has been related to the formation of dimers as premicellar aggregates (González-Perez et al. 2004; Blanco et al. 2005).

Solution density is calculated as function of composition using Eq. 6 with $m_3 = 0$. Figure 1 shows the agreement between model results and experimental density values from this study. We have extrapolated the calculations up to $x_2 \sim 1$, in order to estimate the surfactant density $\rho_2$ in a hypothetical pure liquid state ($x_2 = 1$) as $\rho_2 = \rho(x_2 = 1)$. Results
are shown in Fig. S8 of the supporting information. The values obtained at 296.15 K are 1122.12 kg m\(^{-3}\), 1101.51 kg m\(^{-3}\), 1060.75 kg m\(^{-3}\) and 1175.15 kg m\(^{-3}\) for NaOct, NaDec, NaDod and NaDS, respectively. The corresponding surfactant molecular volumes calculated from these results are 0.246 nm\(^3\), 0.293 nm\(^3\), 0.348 nm\(^3\) and 0.408 nm\(^3\). (Rodríguez-Pulido et al. 2010) estimated the surfactant molecular volume in micelles from experimental data at 298.15 K as 0.297 nm\(^3\) and 0.35 nm\(^3\) for NaDec and NaDod. Mazer et al. (1976) reported a value of 0.526 nm\(^3\) for NaDS.

Our calculated molecular volumes for the extrapolated pure liquid surfactants are quite similar to ones for the micellar pseudo-phase (considering micelles as a pure substance). Differences may likely reflect the constraints on molecular orientation introduced by the confined micellar structure, compared to the bulk liquid. We therefore take the extrapolated values for a hypothetical pure liquid surfactant state to represent mean values for the possible surfactant aggregates. NaOct aggregation numbers vary between 11 and 26 depending on the concentration (Gonzalez-Perez et al. 2003), whereas the estimated micelle aggregation numbers are 47 and 89 molecules for NaDec and NaDod (Rodríguez-Pulido et al. 2010). On the other hand, Medoš and Bešter-Rogač (2017) found that the two-stage micellization of NaOct and NaDec in aqueous solutions at 298.15 K can be represented by aggregation numbers of 3 and 11, 8 and 29; respectively; while for NaDod there is a single-stage process with an aggregation number of 21. The average aggregation number for NaDS in aqueous solutions at the CMC and at 298.15 K is 64 (Mazer et al. 1976; Duplâtre et al. 1996).

### 4.2 Ternary solutions

Densities for ternary solutions were calculated from Eq. 6 using Young’s mixing rule, Eq. 4, for the apparent mean molar volume of surfactant and salt solute. In this framework, we assessed the suitability of three different models for the apparent molal volumes of the

| Model used for binary salt system | \(r^2\) | \(\text{SSE}^a\) (kg m\(^{-3}\)) | \(\text{MSSE}^a\) (kg m\(^{-3}\)) |
|----------------------------------|-------|----------------|----------------|
| NaOct–NaCl (\(N=26\), this work). Temperature used in calculations: 299.15 K | | | |
| Rogers and Pitzer (1982) | 0.9988 | 0.9955 | 4.78 38.34 | 0.19 1.37 |
| Archer (1992) | 0.9985 | 0.9940 | 5.96 51.78 | 0.24 1.85 |
| Rowe and Chou (1970) | 0.9981 | 0.9941 | 7.44 50.53 | 0.30 1.81 |
| NaDec–NaCl (\(N=26\), this work) Temperature used in calculations: 300.15 K | | | |
| Rogers and Pitzer (1982) | 0.9945 | 0.9507 | 3.69 33.30 | 0.15 1.33 |
| Archer (1992) | 0.9941 | 0.9398 | 3.95 40.61 | 0.16 1.62 |
| Rowe and Chou (1970) | 0.9918 | 0.9307 | 5.53 19.39 | 0.22 1.87 |
| NaDod–NaCl (\(N=40\), this work) Temperature used in calculations: 302.15 K | | | |
| Rogers and Pitzer (1982) | 0.9290 | 0.3128 | 13.30 128.71 | 0.34 3.30 |
| Archer (1992) | 0.9276 | 0.2709 | 13.55 136.56 | 0.35 3.50 |
| Rowe and Chou (1970) | 0.6146 | -0.3841 | 72.19 259.24 | 1.85 6.65 |
| NaDS–NaCl (\(N=78\) Kushner et al. 1952) Temperature used in calculations: 296.15 K | | | |
| Rogers and Pitzer (1982) | 0.9957 | | 0.66 | 0.009 |
| Archer (1992) | 0.9921 | | 1.21 | 0.016 |
| Rowe and Chou (1970) | 0.9598 | | 6.94 | 0.090 |

\(a:\ r^2\), correlation coefficient; \(\text{SSE}\), sum of squared errors; \(\text{MSSE}\), mean of the squared of the errors
surfactant and the salt in their respective binary solutions, specifically the models from Rogers and Pitzer (1982) Eq. 14, Archer (1992) Eq. S11 and Rowe and Chou (1970) Eq. S12 and Eq. S13. Statistical indicators for the model performance against experimental density data are given in Table 3. Residuals patterns in terms of the surfactant molality are provided in the supporting information. With the exception of NaDod–NaCl solutions, our model is able to capture more than 93% of the experimental variance with mean values of the sum of squared errors (MSSE) below 1.9 kg m$^{-3}$. Our model performs less well for NaDod–NaCl solutions, where MSSE can be as high as 6.7 kg m$^{-3}$. In all cases, MSSE values are significantly higher than uncertainties of the experimental measurements, 3 × 10$^{-2}$ kg m$^{-3}$, and 1.5 × 10$^{-1}$ kg m$^{-3}$, for pyknometers of 50 mL and 10 mL of capacity, as is shown in the supporting information.

For NaDS–NaCl aqueous solutions, the calculated densities at 296.15 K match the experimental values reported by Kushner et al. (1952) at the same temperature. The statistical indicators in Table 3 indicate a good agreement. In Fig. 2, we show the calculated and measured density values accompanied by the variation of CMC$^{\text{rer}}$ as function of salt molality to highlight the model performance in relation to micellization. All experimental points with surfactant concentrations above CMC$^{\text{rer}}$ (found to the right of the black dots) represent aqueous systems containing a micelle pseudo-phase. Calculated densities agree very well with experimental observations, both below and above the CMC$^{\text{rer}}$, suggesting that our model is able to capture the changes on the surfactant micellization induced by the added salt. The best results of our model are found with the apparent partial molal volume of the inorganic salt as given by Rogers and Pitzer (1982). CMC$^{\text{rer}}$ values were calculated using Eq. S15.

In general, for a given surfactant concentration $m_2$, the solution density increases with decreasing surfactant–salt mass mixing ratio. Similarly, at a fixed surfactant–salt mass mixing ratio, the solution density increases with increasing surfactant concentration. The good agreement between calculated and experimental values suggests that our framework is able to capture the deviations from the ideal behaviour in ternary solutions using Fig. 2

Fig. 2 Densities of aqueous solutions containing NaDS and NaCl at 296.15 K as function of the surfactant molality $m_2$ for different NaCl molalities $m_3$. Experimental values from Kushner et al. (1952) are compared to model results. CMC$^{\text{rer}}$ values were calculated using Eq. S15.
just binary water–salt and water–surfactant interactions. At these conditions, there are no significant effects of water–salt–surfactant interactions beyond those captured by the Debye–Pitzer–Hückel theory.

For the rest of the systems, NaOct–NaCl, NaDec–NaCl and NaDod–NaCl, the calculated densities at 296.15 K show the same composition-dependence of the experimental data with increasing surfactant and inorganic salt concentrations in solution. The best results were obtained with the modified model of Rogers and Pitzer (1982) for the apparent molal volume of NaCl. However, the model overestimates the experimental values in all cases, with mean positive deviations of +1.37 kg m\(^{-3}\), +1.33 kg m\(^{-3}\) and 3.3 kg m\(^{-3}\) for aqueous solutions of NaOct–NaCl, NaDec–NaCl and NaDod–NaCl, respectively. It should be noted, however, that the trend of the experimental densities does not converge to the density of pure water at infinite dilution. The measurements are used only to test the performance of the model, and are therefore independent from model results. Our thermodynamic framework is based on Debye-Hückel theory, which uses the infinite dilution as reference state and model calculations are therefore valid and considered fully reliable for highly dilute solutions. This suggests the possible presence of artefacts in the experimental densities contributing to their discrepancies with respect to model results.

Agreement between calculations and experiments was less satisfactory for aqueous solutions of NaDod–NaCl. One factor could be the low solubility of NaDod in water. Aqueous solubility of sodium dodecanoate is 1–2 orders of magnitude lower than solubilities for sodium octanoate and sodium decanoate (Eggenberger et al. 1949). This introduces additional challenges in preparing solutions with well-constrained concentrations in the dilute

![Fig. 3](image-url)  
Fig. 3 Densities for aqueous solutions of NaOct and NaCl at 299.15 K as function of the surfactant molality \(m_2\) at different surfactant/salt mass ratios \(w_2/w_3\). Experimental values are compared to model results. CMC\(_{\text{ter}}\) values were calculated with Eq. 11.
pre-micellar region. Concentration artefacts relating to the organic surfactant content may introduce biases in the mixing ratios between low-solubility surfactant and highly soluble salt in the solutions. However, this does not explain why our measured density values cannot be extrapolated to the density of pure water at the infinite dilution limit. The measured densities were obtained independently and should converge to the density of pure water when the surfactant concentration decreases after several dilution steps. Our density measurements and those from Álvarez-Silva et al. (2010) for binary solutions of sodium dodecanolate did not reproduce a linear relationship between the surfactant apparent molal volume and the surfactant molality at concentrations below 0.01 M.

Another potential source of artefacts relate to the slight heating of some of the most concentrated solutions to ensure complete dissolution of surfactant solutes. As we perform the measurements in a dilution series, it is possible that the solution temperature has not fully equilibrated with the room temperature for the first and most concentrated solutions at the time of measurement. This means that experimental density values correspond to slightly elevated temperatures, compared to the nominal temperature of the experiments. Again, this bias would not be significant for the most dilute solutions, for which measurements were typically performed more than 10 hours after preparation of the concentrated stock solution.

We explored possible causes of the positive biases observed between the measured densities and calculated values at 296.15 K, by testing the model sensitivity to changes in both experimental parameters and model inputs. The existence of positive biases of similar magnitude between the calculated and measured densities suggests the existence of systematic errors. We studied the influence of the three independent variables used in calculations, the temperature, the surfactant/salt mass mixing ratio of the solution and the parametrization

![Fig. 4](https://example.com/fig4.png)  
**Fig. 4** Densities for aqueous solutions of NaDec and NaCl at 300.15 K as function of the surfactant molality $m_2$ at different surfactant/salt mass ratios $w_2/w_3$. Experimental values are compared to model results. CMCter values were calculated with Eq. 11.
used to represent the pure water density. The modeling of the density of aqueous electrolyte solutions relies on the fundamental assumption that the nonsolvated water molecules occupy a molar volume equal to that of the pure water and that all solution nonidealities are captured by the apparent partial molal volume of the solute. The full analysis is described in the supporting information.

During the sensitivity analysis, we discarded the surfactant–salt mass mixing ratio and the parametrization of the pure water density as sources of artefacts. We noticed a minimum value for the mean of the modeling errors when the densities of our aqueous solutions of NaOct–NaCl, NaDec–NaCl and NaDod–NaCl were calculated at 299.15 K, 300.15 K and 302.15 K, respectively. In Table 3 we show how using these temperatures in calculations, there are significant improvements for all the statistical indicators of the goodness of the fitting (e.g., the maximum value for the MSSE becomes 0.34 kg m\(^{-3}\) for NaDod–NaCl solutions, a value that is only twice the experimental uncertainty for the measurement of the density using a 50 mL-volume pyknometer). These results indicate that the temperature of the solution is the most prominent potential source of experimental bias.

Results for aqueous NaOct–NaCl solutions at 299.15 K are shown in Fig. 3, where we observe how the solution density increases with increasing surfactant concentrations and decreasing surfactant/salt mass ratios. Calculated density values follow the trend in experimental measurements both below and above CMC, at all surfactant/salt mass mixing ratios.

Figure 4 shows results for aqueous NaDec–NaCl solutions using 300.15 K as the temperature in the calculations, while the Fig. 5 shows the results for aqueous solutions of NaDod–NaCl at 302.15 K. As it was observed for NaOct–NaCl solutions, the model...
predicts increasing solution density with increasing surfactant molality and decreasing surfactant/salt mass fraction ratio. Our calculated densities follow the trend of the experimental observations both below and above CMC. The model is able to represent the effect of the variation in the surfactant/salt mass mixing ratio between the limits of inorganic salt enriched solutions and organic enriched solutions. The consideration of the changes induced by the inorganic salt on the surfactant aggregation (reduction of the micellization parameters, CMC, molar volume change during micellization and the degree of the counterion binding coefficient) was fundamental for the successful implementation of the Young’s mixing rule using binary data for the water–salt and the water–surfactant systems.

It is expected to have a salting-out effect of sodium chloride on sodium dodecanoate aqueous solutions (Michailoudi et al. 2020). At constant composition, this effect causes an increase in the surfactant Krafft temperature. There are different values reported in literature for the Krafft temperature of NaDod in aqueous solutions. Blanco et al. (2005) used the IUPAC definition (Everett 1972) and derived a value equal to 291.45 K from electrical conductivity measurements. On the other hand, Lin et al. (2005) used a different definition and reported a Krafft temperature of 298.15 K equivalent to the clearing temperature of an aqueous 1% wt. surfactant solution. The nominal temperature of our experiments is 296.15 K.

When experiments are performed at constant temperature, the salting-out effect of sodium chloride causes a reduction in the surfactant solubility. Solubility values for aqueous solutions of sodium fatty acid salts mixed with sodium chloride and other inorganic salts were recently calculated with COSMOTHERM as reported in Table 4 (Michailoudi et al. 2020). Sodium dodecanoate mole fractions in our binary water–surfactant solutions vary between $x_2 = 1.37 \times 10^{-5}$ and $x_2 = 3.91 \times 10^{-4}$. In all cases, the surfactant concentration in solution is above the solubility limits at 293.15 K or 298.15 K. Sodium dodecanoate mole fractions in our ternary water–surfactant–inorganic salt solutions vary between $x_2 = 5.83 \times 10^{-5}$ and $x_2 = 3.83 \times 10^{-4}$, while sodium chloride mole fractions are always below $x_3 = 3.9 \times 10^{-3}$.

At the nominal temperature of the experiments (296.15 K), it is very likely that our surfactant concentration was above the solubility limit. Surfactant molecules could have formed an additional phase due to this restriction. However, as the pseudo-phase separation method uses the same model parameter ($\phi_{2,\text{CMC}}$, apparent partial molal volume of the surfactant after micellization) to account for the volume of any excess surfactant concentration above CMC, this extra-phase is already included in calculations at the nominal concentrations.

**Table 4** Solubility values expressed as mole fraction of the surfactant in solution for the studied fatty acid sodium salts

| Solubility (units) | NaOct | NaDec | NaDod |
|--------------------|-------|-------|-------|
| Experimental, in pure water @293.15 K\(^1\) | $8.67 \times 10^{-5}$ | $1.39 \times 10^{-5}$ | $4.46 \times 10^{-6}$ |
| Calculated, in pure water @298.15 K\(^2\) | $1.51 \times 10^{-4}$ | $1.67 \times 10^{-5}$ | $5.20 \times 10^{-7}$ |
| Calculated, in aqueous solution of NaCl at $x_3 = 0.01$ @298.15 K\(^2\) | $9.21 \times 10^{-5}$ | $8.84 \times 10^{-6}$ | $2.42 \times 10^{-7}$ |
| Calculated, in aqueous solution of NaCl at $x_3 = 0.05$ @298.15 K\(^2\) | $1.25 \times 10^{-5}$ | $7.35 \times 10^{-7}$ | $5.50 \times 10^{-8}$ |
| Calculated, in aqueous solution of NaCl at $x_3 = 0.10$ @298.15 K\(^2\) | $1.48 \times 10^{-6}$ | $5.50 \times 10^{-8}$ | – |

\(^1\) Weast (1989)

\(^2\) Michailoudi et al. (2020)
Experimentally determined densities were used only to test the performance of our model. The model derivation or the values of model parameters are obtained completely independently from the measured densities. The scatter of experimental values is greatest for the least soluble and most difficult to handle surfactant NaDod. The possible sources of experimental uncertainty are discussed above and mainly relate to the determination of sample concentration for very dilute solutions of the surfactant with the most limited aqueous solubility.

In principle the model can be applied for full composition range from pure water to pure surfactant because above CMC all of the different aggregate forms are represented with a single molar volume which is the hypothetical molar volume of the pure surfactant. Data is needed to validate the quality of the predictions with the model in the extreme composition ranges of pure surfactant, where currently measurements are not available.

5 Conclusions

We present a model to calculate the density of aqueous surfactant–salt solutions with composition-dependent functions that vary continuously along the composition range and take into account surfactant–salt interactions during micellization. The calculation framework was validated against experimental densities for aqueous solutions of sodium chloride mixed with one of surfactant sodium salts, NaOct, NaDec, NaDod or NaDS. The framework enables prediction of ternary solution density using the apparent partial molal volumes of the surfactant and salt calculated as a function of the salt concentration for binary aqueous solutions of the same total molality and CMC\textsuperscript{ter} values. The model can be generally applied to describe other surfactant–salt solutions, and extended to include the formation of mixed micelles with a composition-dependent function for the solution CMC.

This is a great advantage for subsequent applications to predictions of surfactant-containing droplet growth and activation, mimicking atmospheric cloud formation processes, since both variables can be measured experimentally in an easier way than other properties typically used to assess deviations from ideal solution interactions.

Nevertheless, in the atmosphere much more complex surfactants are present. For example, biosurfactants, such as viscosin, massetolide E and syringafactin A, were isolated and identified by LC-MS-MS in cloud water samples. These linear and cyclic lipopeptides are secondary metabolites of microbial strains (e.g. *Pseudomonas* and *Xanthomonas* strains). They have high molecular weight and strong surface activity, as evidenced by their low concentrations and low surface tension values at the observed CMC. For example, the CMC of viscosin is 23.1 μmol L\textsuperscript{−1} and the surface tension at CMC is 25 mN m\textsuperscript{−1} (Renard et al. 2019). The task of modeling the density of biosurfactants in aqueous solutions will be the focus of future work. Among the challenges to be addressed in this respect are obtaining sufficiently well-defined concentration dependent CMC in surfactant solutions containing also inorganic salts of atmospheric relevance, as well as density measurements in the pre-micellar and post-micellar concentration ranges. The exploration of the properties of the micellar phase (e.g. aggregation number and degree of counterion binding) with spectroscopic methods (e.g. nuclear magnetic resonance, fluorescence anisotropy and fluorescence correlation spectroscopy) could also be helpful in this regard (e.g. Furó 2005; Gehne et al. 2013).

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Compliance with Ethical Standards

Conflict of interests The authors declare that they have no conflict of interest.

Supporting information The supporting information file contains the following sections:
- Critical micelle concentration in aqueous surfactant solutions.
- Modeling approach for the apparent partial molal volume of sodium chloride in aqueous solutions.
- Experimental densities for aqueous surfactant salt solutions.
- Uncertainty in density measurements.
- Uncertainties related to the reagents.
- Density of pure surfactant as hypothetical subcooled liquids.
- Model sensitivity.

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