Solubility and Activity Coefficients of Atmospheric Surfactants in Aqueous Solution Evaluated Using COSMOtherm

Georgia Michailoudi,[†] Noora Hyttinen,[†,‡] Theo Kurtén,[‡] and Nønne L. Prisle[*,†]

†*Nano and Molecular Systems Research Unit, University of Oulu, P.O. Box 3000, FI-90014 Oulu, Finland*

‡*Department of Chemistry and Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland*

E-mail: nonne.prisle@oulu.fi

Abstract

Fatty acids ($CH_3(CH_2)_{n-2}COOH$) and their salts are an important class of atmospheric surfactants. Here, we use COSMO*therm* to predict solubility and activity coefficients for C_2–C_{12} fatty acids with even number of carbon atoms and their sodium salts in binary water solutions and also in ternary water–inorganic salt solutions. COSMO*therm* is a continuum solvent model implementation which can calculate properties of complex systems using quantum chemistry and thermodynamics. Calculated solubility values of the organic acids in pure water are in good agreement with reported experimental values. The comparison of the COSMO*therm* derived Setschenow constants for ternary solutions comprising NaCl with the corresponding experimental values from literature shows that COSMO*therm* overpredicts the salting out effect in all cases except for the solutions of acetic acid. The calculated activity and mean activity coefficients of fatty acids and fatty acid sodium salts, respectively, show deviation of the systems from ideal solution. The computed mean activity coefficients of the fatty acid salts in binary systems are in better agreement with experimentally derived values for the organic salts with longer aliphatic chain (C_8–C_{10}). The deviation of the solutions from ideality could lead to biased estimations of cloud condensation nuclei number concentrations if not considered in Köhler calculations and cloud microphysics.

Introduction

Atmospheric aerosols have both direct and indirect effects on the radiating forcing of the atmosphere. The direct effects include the absorption and scattering of solar radiation while the indirect effects of aerosols are related to their role in cloud formation, acting as cloud condensation nuclei (CCN).[1] Organic compounds are a significant fraction of atmospheric aerosols and, depending on the geographical location, can cover 20 to 90% of their total mass.[2–4]

Fatty acids ($CH_3(CH_2)_{n-2}COOH$) are common constituents of organic aerosols and they

have been found in concentrations up to a few μgm^{-3} in urban regions,[5,6] in concentrations of several ngm^{-3} in continental regions[7–9], and in lower concentrations in marine environments.[10,11] In marine environments, they can be emitted, for example, into the marine air during bubble bursting processes (sea spray)[12–14] and are typically in their ionic forms[15] as they can dissociate in water ($pK_a < pH_{water}$). The carboxylate anion ($CH_3(CH_2)_{n-2}COO^-$) can be bound to a sodium cation, resulting in fatty acid sodium salts ($CH_3(CH_2)_{n-2}COONa$).

In addition to being a common and abundant class of atmospheric organic aerosol, both fatty acids and their salts are known to act as surfactants in aqueous solutions and they are relatively well–characterized in terms of their amphiphilic behaviour[16,17] and cloud forming properties.[18–22] They are therefore often used as model system for atmospheric surface active aerosol, although the extent of how well they represent all of these remains to be firmly established.[23] Amphiphilic compounds are partly hydrophobic (the aliphatic chain of a fatty acid) and partly hydrophilic (the carboxylic acid group) and they can affect the surface tension of aqueous solutions.[19,24] Surface activity can affect water uptake and cloud droplet activation, introducing uncertainty in climate predictions. Köhler theory[25] describes the CCN activation in terms of the properties of the droplet bulk solution, among them the water activity and the surface tension. For a better understanding of the role of surfactants in cloud microphysics, experimental and theoretical studies have investigated the physico-chemical properties of these compounds.[18,24]

When organic surfactants and inorganic salts are in an aqueous solution, salting in/out interactions between the organic and inorganic components can occur. Salting in/out phenomena in aqueous solutions are here defined as changes in the solubility of the organic compound due to the presence of the inorganic salt in the solution.[26–28] Most studies have considered the water-surfactant solutions as ideal, such that all the activity coefficients have been assumed to be 1. Activity coefficients can be used to illustrate the deviation from ideality but they cannot be measured easily for atmospherically relevant aqueous mixtures and they are not typically available in literature. This limits the understanding of microscopic

3

interactions in solutions of higher order than binary, where Gibbs-Duhem relation cannot be used to infer organic activity from water activity measurements that are easier to be determined experimentally. COSMO*therm*,[29] combining quantum chemistry and thermodynamics, can predict thermodynamic properties of molecules in liquid environments. Here we use COSMO*therm* to calculate the solubilities and activity coefficients of fatty acids in binary aqueous solutions and ternary solutions comprising inorganic salts in order to examine the salting in/out interactions between the components and to investigate the deviation of the solutions from the ideal solution behavior. Solubilities and activity coefficients were also calculated for the corresponding sodium salts. We present calculated solubility and activity coefficient data over a range of aqueous solution compositions, and discuss the implications of the predicted deviations from ideality for aerosol and cloud activation properties.

Methods

We calculate the solubilities and activity coefficients of C_2–C_{12} fatty acids with even number of carbon atoms and their sodium salts in pure water and ternary aqueous mixtures comprising different inorganic salts using the COSMO*therm* program release 19.[29] The inorganic salts in the aqueous ternary systems are sodium chloride (NaCl), ammonium chloride (NH_4Cl), ammonium sulfate (($NH_4)_2SO_4$), sodium sulfate (Na_2SO_4) and ammonium nitrate (NH_4NO_3). The chemical formulae of the organic acids are presented in Table 1.

Table (1) **Summarized studied organic acids.**

Compound	Formula
Acetic acid	CH_3COOH
Butanoic acid	$CH_3(CH_2)_2COOH$
Hexanoic acid	$CH_3(CH_2)_4COOH$
Octanoic acid	$CH_3(CH_2)_6COOH$
Decanoic acid	$CH_3(CH_2)_8COOH$
Dodecanoic acid	$CH_3(CH_2)_{10}COOH$

The input files for the COSMO*therm* calculations were generated using the systematic calculation scheme described by Kurtén et al.[30] In the calculation scheme, a systematic

conformer sampling was performed using the Spartan '14 program[31] and the MMFF94 force field. The COSMO*conf* program, version 4.1[32] was used for the geometry optimizations and identifying, for example, duplicate conformers. All of the initial conformers from Spartan were optimized at the BP/def-SV(P) level of theory, after which duplicate conformers and conformers with similar chemical potentials were removed, and the number of conformers was limited to 600. The remaining conformers were further optimized at the BP/def-TZVP level of theory and again similar conformers based on their geometries and chemical potentials were removed. Up to 500 lowest energy conformers were selected for the final single-point calculation at the BP/def2-TZVPD-FINE level of theory. In COSMO*therm* calculations we used the fifty lowest energy conformers of each compound due to computational limitations.

Aqueous solubility

To calculate organic solubility, COSMO*therm* finds the liquid-liquid or solid-liquid equilibrium of each solute in the solution using the solid-liquid equilibrium solver (SLESOL). To find the liquid-liquid equilibrium, COSMO*therm* solves the equation:

$$x_j^1 \gamma_j^1 = x_j^2 \gamma_j^2 \tag{1}$$

where x_j^1, γ_j^1 and x_j^2, γ_j^2 are the mole fractions and activity coefficients of two liquid phases (1 and 2) for a compound j, respectively.

In a system with pressure P and temperature T, the solubility of a solid solute j in a solvent is defined as:

$$\log_{10}(x_j^{SOL}) = \frac{\mu_j^{*(I,\circ)}(T,P) - \mu_j^{*(I)}(T,P,x_j^{SOL}) - \max(0, \Delta G_{fus}(T))}{RT \ln(10)} \tag{2}$$

where $\mu_j^{*(I,\circ)}$ is the calculated pseudo-chemical potential of the pure compound j, $\mu_j^{*(I)}$ is the pseudo-chemical potential of the solute j at the solubility limit composition (x_j^{SOL}), ΔG_{fus} the free energy of fusion of the solute and R is the gas constant. In this study, the

temperature was set to 298.15 K for all the calculations.

For solid solutes, either the ΔG_{fus}, or the melting point (T_{melt}) and the enthalpy of fusion (ΔH_{fus}) of the solute must be given as input. In our calculations we used the T_{melt} and ΔH_{fus} values for the solid solutes, i.e. decanoic and dodecanoic acid as well as the sodium organic salts of the fatty acids (Table 2). To the best of our knowledge, experimental ΔH_{fus} values for sodium hexanoate, sodium octanoate, sodium decanoate and sodium dodecanoate are not reported in the literature, and we made the approximation that these values are identical to that of sodium butanoate. In case of liquid pure solutes (C_2–C_8 fatty acids) COSMO*therm* assumes that $\Delta G_{fus} = 0$.

Table (2)   Melting point (T_{melt} in °C) and enthalpy of fusion (ΔH_{fus} in kJ/mol) of the studied solid organics.

Organic	T_{melt} [°C]	ΔH_{fus} [kJ/mol]
$CH_3(CH_2)_8COOH$	31.4 [a]	28.05 [b]
$CH_3(CH_2)_{10}COOH$	43.8 [a]	36.03 [b]
CH_3COONa	328.2 [a]	17.95 [c]
$CH_3(CH_2)_2COONa$	252 [d]	10.418 [c]
$CH_3(CH_2)_4COONa$	232 [e]	-
$CH_3(CH_2)_6COONa$	243-245 [f]	-
$CH_3(CH_2)_8COONa$	248-250 [f]	-
$CH_3(CH_2)_{10}COONa$	244-246 [f]	-

[a] CRC Handbook of Chemistry and Physics (2004)[33] [b] Arpe et al. (1992)[34] [c] Ferloni et al. (1975)[35] [d] Duruz et al. (1971)[36] [e] Michels et al. (1972)[37] [f] Zacharie et al. (2009)[38]

Dissociation correction

When fatty acids are dissolved in water, they dissociate partially into their constituent ions. The dissociation can affect the solubility of the compound. For comparison, the dissociation corrected solubilities of pure fatty acids in water were calculated by taking into account the acid dissociation constant (pK_a) and were compared to the corresponding COSMO*therm* derived solubilities without the dissociation correction and experimental values from literature. Due to lack of experimental values for these binary mixtures at 298.15 K, all the above-mentioned solubilities were calculated at 293.15 K in order to be comparable with the

experimental values.

The experimental solubilities and the acid dissociation constants of the compounds are summarized in Table 3.

Table (3) Experimental solubility values (S_0) [g/100g of water] of fatty acids in water at 293.15 K and acid dissociation constants (pK_a) of the solutions.

Acid	S_0 [g/100g]	pK_a
CH_3COOH	soluble [a]	4.756 (298.15 K) [b]
$CH_3(CH_2)_2COOH$	soluble [a]	4.83 (298.15 K) [b]
$CH_3(CH_2)_4COOH$	0.967 [b]	4.85 (298.15 K) [b]
$CH_3(CH_2)_6COOH$	0.08 [b]	4.89 (298.15 K) [b]
$CH_3(CH_2)_8COOH$	0.015 [b]	4.9 (298.15 K) [c]
$CH_3(CH_2)_{10}COOH$	0.0055 [b]	5.3 (293.15 K) [d]

[a] Perry's Chemical Engineers' Handbook[39] [b] CRC Handbook of Chemistry and Physics (2004)[33] [c] Barratt et al. (1996)[40] [d] Serjeant and Dempsey (1979)[41]

The dissociation corrected (DC) solubility in mole fraction is:

$$x^{DC} = x_j^{SOL} + x_{A^-}, \tag{3}$$

where x_{A^-} is the mole fraction of the dissociated ionic species, given from the equation:

$$x_{A-} = \frac{c_{A^-} \cdot M}{\rho} \tag{4}$$

M and ρ are the molecular weight (g/mol) and density of water (g/l), respectively, and:

$$c_{A^-} = -\frac{1}{2}10^{-pH} + \sqrt{\frac{1}{4}10^{-2pH} + c_j^{SOL}10^{-pK_a}} \tag{5}$$

The pH corresponds to the aqueous phase and the mole fractions x_j^{SOL} are converted to molar concentration c_j^{SOL}:

$$c_j^{SOL} = x_j^{SOL}\frac{\rho}{M} \tag{6}$$

Ternary solutions

In ternary systems, we consider the mixture of water and an inorganic salt as one solvent, as opposed to solvent water and an inorganic salt solute. The mole fraction of the inorganic salt ($M_{\nu+}X_{\nu-}$) in the solvent is defined by the mole fractions of its anion (x_{X-}) and cation (x_{M+}) and not by the mole fraction of the formula unit of the salt. This means that the total molar size of the system in the COSMO*therm* framework is larger than the size of a system where the inorganic salt is considered as entity in the solvent. In order to calculate the solubility x'_j of the latter solvent-solute system, we scale the solubility of the COSMO*therm* framework with the molar size of this system at the solubility limit:

$$x'_j = \frac{x_j^{SOL}}{1 - (1 - x_j^{SOL})x_{M+}} \tag{7}$$

Here we assume that the number of negative ions (ν^-) is 1.

Setschenow constants

Salting-in or -out of the organic by presence of inorganic salts can be described using the Setschenow constant (K_s in units of l/mol):

$$\log(\frac{S_0}{S}) = K_s c_{MX} \tag{8}$$

where S_0 and S are the solubilities of the organic compound in pure water and in aqueous inorganic salt mixture, respectively, and c_{MX} is the concentration of the salt. Negative and positive values of the Setschenow constants indicate a salting-in and salting-out effect, respectively.

To the best of our knowledge, from the ternary solutions of the fatty acids that we study here, the available experimental values of K_s in literature are limited to acetic, butanoic and hexanoic acid with NaCl. To evaluate our results we translated the computed solubility to the Setschenow constants and we compared them to the experimental K_s values. The mole

fraction of salt (x_{MX}) was converted to molar concentration (mol/l):

$$c_{MX} = x_{MX}\frac{\rho}{M},\tag{9}$$

where ρ here is the density of the binary water-sodium chloride solution and M is the average molecular mass of the binary solution. The binary salt solution density ρ was estimated at the temperature of 298.15 K and pressure of 1 atm from the formula given by Rowe et al.[42] (description is provided in the Supporting Information). This formula is valid for mole fraction of NaCl up to 9.32% (25% mass fraction of salt in water) and for that reason we only calculated the K_s for 1% and 5% mole fraction of NaCl.

Relative solubility of sodium salts

In the ternary systems, the solubilities of the fatty acid salts were calculated using the relative screening method of COSMO*therm*. With this approach, the solubility of the solute in a solvent mixture is calculated relative to the solubility in a reference solvent, as opposed to an absolute value. With the relative solubilities it is possible to estimate the salting effect of the different inorganic salts for the solutes that are otherwise fully miscible with the solvent. In addition, the relative solubilities are calculated using the zeroth order approximation of the solubility, where the free energy of fusion cancels out. In the zeroth order approximation the solubility is given as:

$$\log_{10}(x_j^{SOL(0)}) = \frac{\mu_j^{*(I,\circ)}(T,P) - \mu_j^{*(I)}(T,P,x_j \to 0) - \max(0,\Delta G_{fus})}{RT\ln(10)}\tag{10}$$

The solubility of the solute in the solvent is assumed to be small enough to justify the use of the chemical potential of the solute at infinity dilution $(\mu_j^{*(I)}(T,P,x_j \to 0))$ instead of the chemical potential in the solubility limit $(\mu_j^{*(I)}(T,P,x_j^{SOL}))$.

To estimate the absolute solubility of the solute in mixed binary solvents, the values were referenced to the absolute SLESOL solubility of the solute in 0.09 mole fraction of inorganic

salt. We selected a high mole fraction of salt as some of the fatty acids are fully miscible in solutions with lower mole fractions of the inorganic salts. Using 0.09 mole fraction of the inorganic salts in the solvent, none of the fatty acids are fully miscible, so COSMO*therm* could give an absolute value of solubility. After the above process, the values of solubility are re-calculated relative to the solubility of the solute in pure water.

Hydrated sodium

In COSMO*therm*, solute salts are described as individual ions. For example, the fatty acid sodium salts require separate cosmo-files for the sodium cation (Na^+) and the carboxylate anion ($CH_3(CH_2)_{n-2}COO^-$). Previous studies[43,44] have shown that COSMO*therm* cannot predict the properties of a solution that contains strong electrolytes, such as the sodium cation. Toure et al. have used hydrated forms of strong monoatomic ions to better predict the ion–molecule and molecule–molecule interactions in electrolyte solutions.[43,44] Here, we tested the effect of solvating sodium cation of the organic salts with up to five water molecules ($Na \cdot (H_2O)_k$, with $k = 0, 1, 2, 3, 4$ or 5) on the relative solubilities of the organic salts. An additional correction should be applied for the calculation of the solubility value (x_j') as the water molecules of the hydrated sodium cation change the mole fraction of water and therefore of inorganic salt in the solvent. With the addition of the hydrated solute to the system, the amount of solution increases from 1 to $1 + k \cdot x_j'$ and the solubility x_j'' of the dry fatty acid sodium salt is:

$$x_j'' = \frac{x_j'}{1 + kx_j'} \tag{11}$$

In binary solutions, $x_j' = x_j^{SOL}$.

Activity coefficients

For the calculation of activity coefficients on mole fraction scale for each solute (fatty acid/fatty acid salt) in a hypothetical infinite dilution state, the mole fraction of the solute is set to zero in the composition of the solution and the reference state is the pure solute. COSMO*therm* calculates the natural logarithmic values of the activity coefficient using the pseudo-chemical potentials of the compound both in its pure form, and fully dissolved in a solvent.

$$\ln(\gamma_j^{\mathrm{I}}) = \frac{\mu_j^{*(\mathrm{I})}(T, P, x_j) - \mu_j^{*(\mathrm{I},\circ)}(T, P)}{RT} \tag{12}$$

where $\mu_j^{*(\mathrm{I})}(T, P, x_j)$ the chemical potential of compound j in the solution and $\mu_j^{*(\mathrm{I},\circ)}(T, P)$ the chemical potential of the pure compound j.

Activity coefficients are normalized using the symmetric convention or convention I.[45] In this convention the reference state is an ideal solution where the activity coefficient of any species in the solution tends to the unity when its mole fraction tends to unity. Since electrolytes cannot exist as pure liquids at the solution temperature, activity coefficients in its aqueous solutions are normalized using the unsymmetric convention or convention II.[45] In this convention the reference state is an ideal dilute solution where the activity coefficients are equal to the unity when the molar fraction of the solvent and solute tends to one and zero, respectively. In this condition, the solute activity coefficient is referred as the activity coefficient at infinite dilution. Convention II is easy to use to describe binary systems but requires careful assumptions when it is applied to multicomponent solutions.[46] Here, we will use COSMO*therm* to calculate activity coefficients on convention I below solubility limits and at infinite dilution. Then we will transform their values to convention II in order to compare them against experimental values. Even when the procedure to switch activity coefficients between conventions is widely known[45,47,48] we must show here how to use the pseudochemical potential from COSMO*therm* as an equivalent form of expression

of the chemical potential. In convention I the chemical potential of a compound j at the temperature, pressure and composition x_j of the solution can be written as:[45]

$$\mu_j^{(\mathrm{I})}(T, P, x_j) - RT \ln x_j = \mu_j^{(\mathrm{I},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{I}} \tag{13}$$

where $\mu_j^{(\mathrm{I},\circ)}(T, P)$ is the chemical potential of j as a pure compound at the same temperature, pressure and aggregation state of the solution and γ_j^{I} is the activity coefficient of the compound at the state x_j. In Convention II the chemical potential of j at an equivalent set of conditions can be written as:

$$\mu_j^{(\mathrm{II})}(T, P, x_j) - RT \ln x_j = \mu_j^{(\mathrm{II},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{II}} \tag{14}$$

where $\mu_j^{(\mathrm{II},\circ)}(T, P)$ is the chemical potential of compound j at the same temperature, pressure and aggregation state of the solution but in a hypothetical dilute ideal state and γ_j^{II} is its activity coefficient normalized to convention II. The pseudo-chemical potentials μ^* for conventions I and II are defined as:

$$\mu_j^{*(\mathrm{I})}(T, P, x_j) = \mu_j^{(\mathrm{I})}(T, P, x_j) - RT \ln x_j \tag{15}$$

and

$$\mu_j^{*(\mathrm{II})}(T, P, x_j) = \mu_j^{(\mathrm{II})}(T, P, x_j) - RT \ln x_j \tag{16}$$

respectively. From the eqs 13 and 14 the pseudo-chemical potential for the two conventions can also be expressed as:

$$\mu_j^{*(\mathrm{I})}(T, P, x_j) = \mu_j^{(\mathrm{I},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{I}} \tag{17}$$

and

$$\mu_j^{*(\mathrm{II})}(T, P, x_j) = \mu_j^{(\mathrm{II},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{II}} \tag{18}$$

The activity coefficient calculated in the convention I γ_j^{I} is numerically different from the activity coefficient calculated on the convention II γ_j^{II}, but the chemical potential of j in a solution of composition x_j at temperature T and pressure P is independent of the convention chosen[48,49] and then:

$$\mu_j^{(\mathrm{II})}\left(T, P, x_j\right) = \mu_j^{(\mathrm{I})}\left(T, P, x_j\right) \tag{19}$$

$$\mu_j^{(\mathrm{II})}\left(T, P, x_j\right) - RT \ln x_j = \mu_j^{(\mathrm{I})}\left(T, P, x_j\right) - RT \ln x_j \tag{20}$$

$$\mu_j^{*(\mathrm{II})} = \mu_j^{*(\mathrm{I})} \tag{21}$$

$$\mu_j^{(\mathrm{II},\circ)}\left(T, P\right) + RT \ln \gamma_j^{\mathrm{II}} = \mu_j^{(\mathrm{I},\circ)}\left(T, P\right) + RT \ln \gamma_j^{\mathrm{I}} \tag{22}$$

Both conventions must be identical at the limit of infinite dilution when $x_j \to 0$, $\gamma_j^{\mathrm{II},\circ} = 1$ and $\gamma_j^{\mathrm{I}} = \gamma_j^{\mathrm{I},\infty}$.

When the solute (compound j) is infinitely dilute $(x_j \to 0)$, the pseudo-chemical potential in convention I is:

$$\mu^{*(\mathrm{I})}(T, P, x_j \to 0) = \mu_j^{(\mathrm{I},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{I},\infty} \tag{23}$$

and in convention II the pseudo-chemical potential is:

$$\mu^{*(\mathrm{II})}(T, P, x_j \to 0) = \mu_j^{(\mathrm{II},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{II}} \tag{24}$$

From the eqs 23 and 24 and because by definition the chemical potentials of a compound at the same state are equal $(\mu^{*(\mathrm{I})}(T, P, x_j \to 0) = \mu^{*(\mathrm{II})}(T, P, x_j \to 0))$:

$$\mu_j^{(\mathrm{II},\circ)}(T, P) = \mu_j^{(\mathrm{I},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{I},\infty} \tag{25}$$

Therefore, the eq 18 can be written as:

$$\mu_j^{*(\mathrm{II})}(T, P, x_j) = \mu_j^{(\mathrm{I},\circ)}(T, P) + RT \ln \gamma_j^{\mathrm{I},\infty} + RT \ln \gamma_j^{\mathrm{II}} \tag{26}$$

The equation that relates the activity coefficient of the infinite dilution reference state to the pure-substance reference state can be derived from the eqs 17 and 26:

$$\ln \gamma_j^{\mathrm{I},\infty} + \ln \gamma_j^{\mathrm{II}} = \ln \gamma_j^{\mathrm{II}} \tag{27}$$

Since,

$$\frac{\mu_j^{*(\mathrm{II})}(T, P, x_j) - \mu_j^{(\mathrm{I},\circ)}(T, P)}{RT} = \ln(\gamma_j^{\mathrm{I},\infty} \cdot \gamma_j^{\mathrm{II}}) \tag{28}$$

and

$$\frac{\mu_j^{*(\mathrm{I})}(T, P, x_j) - \mu_j^{(\mathrm{I},\circ)}(T, P)}{RT} = \ln \gamma_j^{\mathrm{I}} \tag{29}$$

are equal, we finally get the equation:

$$\ln \gamma_j^{\mathrm{II}} = \ln \frac{\gamma_j^{\mathrm{I}}}{\gamma_j^{\mathrm{I},\infty}} \tag{30}$$

Ternary solutions

In solutions containing salts, in order to be consistent to the experimental mole fractions of the components, we consider the salt as an entity and not as individual ions. The molar size of the system in COSMO*therm* framework can be scaled to the experimental one by applying a correction for the salt fraction in the solute-solvent system. The mole fraction of a compound j after the correction, is given by:

$$x_j' = \frac{x_j}{1 - x_{M^+}} \tag{31}$$

where x_j and x_j' are the mole fractions of the compound in the COSMO*therm* and experimental framework, respectively.

The activity of the compound j is the same for the two different solute-solvent systems:

$$\alpha_j = x_j' \cdot \gamma_j' = x_j \cdot \gamma_j \tag{32}$$

14

From eqs 31 and 32, the activity coefficient γ'_j was calculated as:

$$\gamma'_j = (1 - x_{M^+})\gamma_j \tag{33}$$

Mean ionic activity coefficients

A strong electrolyte $A_{\nu^+}B_{\nu^-}$, with ν^+ the number of cations A and ν^- the number of anions B, and Z^+ and Z^- the charge of A and B, respectively, dissociates in water:

$$A_{\nu^+}B_{\nu^-} \xrightarrow{H_2O} {}_{\nu^+}A^{Z+} + {}_{\nu^-}B^{Z-} \tag{34}$$

For ionic compounds such as $CH_3(CH_2)_{n-2}COONa$, it is difficult to experimentally estimate the activity coefficient of the anion and cation separately as they dissolve in water. In this case, the deviation from the ideal solution of the electrolyte $A_{\nu^+}B_{\nu^-}$ can be described by the mean ionic activity coefficient $\gamma_{\pm}$:

$$\gamma_{\pm} = \sqrt[\nu^+ + \nu^-]{\gamma_+ \cdot \gamma_-} \tag{35}$$

To be consistent with the common experimental approach, we calculated the mean ionic activity coefficients of the fatty acid sodium salts (C_2–C_{12}) using eq 35, where ν^+ and ν^- are equal to unity.

In case of sodium decanoate, we calculated the mean ionic activity coefficients of the salt in aqueous solutions and compared them with experimentally derived values at 25 °C from the studies of Smith et al.,[50] De Lisi et al.[51] and Sharma et al.[52] Smith et al. applied isopiestic vapour pressure method to calculate osmotic and mean activity coefficients of fatty acid sodium salts. De Lisi et al. calculated the mean activity coefficients from experimentally derived osmotic coefficients using the freezing point technique and available thermodynamic data from previous studies, and Sharma et al. applied mass analysis. In order for our results

to be comparable with the above-mentioned experimental studies, we calculated the mean activity coefficients of sodium decanoate in several states, with the fraction of the sodium decanoate salt set to be within the molal range of these studies, and in infinite dilution state. For the conversion of the $\gamma_\pm$ values from the pure compound reference state (convention I) to the infinite dilution reference state (convention II), we used eq 30. We first calculated the mean ionic activity coefficients having the pure sodium decanoate as the reference state and a state x_i using eq 35. After scaling the mean ionic activity coefficients to the experimental framework by applying eq 33, we divided them with the calculated value with the infinite dilution state mean ionic activity coefficient with pure compound reference state. To scale the mole fractions from COSMO*therm* to the mole fractions of the experimental framework, we apply eq 31.

In order to compare activity coefficients, all of them should be in the same concentration scale. Here, the experimentally derived activity coefficients were in molal basis and we converted them to a mole fraction basis using the equation reported by Prausnitz et al.:[47]

$$\gamma^{(x)} = \gamma^{(m)}(1 + 0.001 \cdot M \cdot m), \tag{36}$$

where $\gamma^{(x)}$ is the activity coefficient in molal basis, $\gamma^{(m)}$ the activity coefficient in mole fraction basis, M the molecular weight (g/mol) and m the concentration of sodium decanoate in $mol \cdot kg^{-1}$.

Following the same process, we compared the calculated mean ionic activity coefficients of sodium acetate, sodium butyrate, sodium hexanoate and sodium octanoate with the values determined by Smith et al.[50]

Ionic strength

Some of the inorganic salts are uni-univalent (e.g. NaCl), while some are divalent-univalent (e.g. Na_2SO_4). The ionic strength of the inorganic salts in the ternary solvents was calculated in order to see the effect of the concentration of dissolved ionic species rather than the

concentration of the salt on the solubility of the studied solutions. The molal ionic strength is given by:

$$I = \frac{1}{2} \sum_{i=1}^{n} b_i (z_i)^2 \tag{37}$$

where b_i is the molal concentration of ion i and z_i is its charge.

Results and discussion

Fatty acids

Solubility

In Figures 1 a-f we present the solubilities (mole fraction) of the organic fatty acids in the studied binary and ternary solutions. In ternary systems (fatty acid–water–inorganic salt), the highest mole fractions of the inorganic salts in the solvent are chosen based on their experimental solubilities in pure water at 20 °C.[33] The numerical solubility values of the fatty acids are presented in Table S1 of the Supporting Information. For all fatty acids, the solubility in pure water is higher than for any of the ternary solutions and shows an increasingly pronounced salting out effect as the mole fraction of the inorganic salt increases. Due to the low solubility of Na_2SO_4 in water, the solubilities of the fatty acids were calculated only for 0.01 mole fraction of the inorganic salt. In the 0.01 mole fraction solvents, Na_2SO_4 gives the lowest solubility of the studied acids compared to the other inorganic salts. For higher inorganic salt mole fractions, solvents with $(NH_4)_2SO_4$ show the strongest salting out effect compared to any of the other inorganic salts. Decanoic and dodecanoic acid are insoluble in 0.1 mole fraction of Na_2SO_4 and dodecanoic acid is insoluble in 0.15 and 0.2 mole fraction of NH_4NO_3. We observe that the salting out effect is getting stronger with the sequence Na_2SO_4, $(NH_4)_2SO_4$, NaCl, NH_4Cl and NH_4NO_3. The same sequence has been observed by Wang et al.[53] when they measured Setschenow constants of organic

compounds in salt solutions. This indicates that COSMO*therm* can capture the effect of specific ion-water interactions in a solution with organic solute. The solubility of the fatty acids decreases with the presence of inorganic salts in the aqueous solution and the salting out effect is stronger, on a mole fraction basis, for inorganic salts comprising polyvalent ions. For a specific mole fraction of an inorganic salt that dissolves in a solvent, the ionic strength of the solution is higher when the salt is composed of polyvalent ions than when it is composed of univalent ions because of the increase of the ionic charge of the solution. Polyvalent ions tend to strongly attract the pair ions that surrounds them and that can lead to stronger interactions between the ions and the polar water molecules. Thus, the lower solubility of the acids in water solutions containing Na_2SO_4 and $(NH_4)_2SO_4$ can be due to less interactions between the water molecules and the molecules of the acid. The solubilities of the fatty acids in the solutions were plotted as a function of the ionic strength (and molal concentration) of the inorganic salts and are presented in Figure S2 of the Supporting Information.
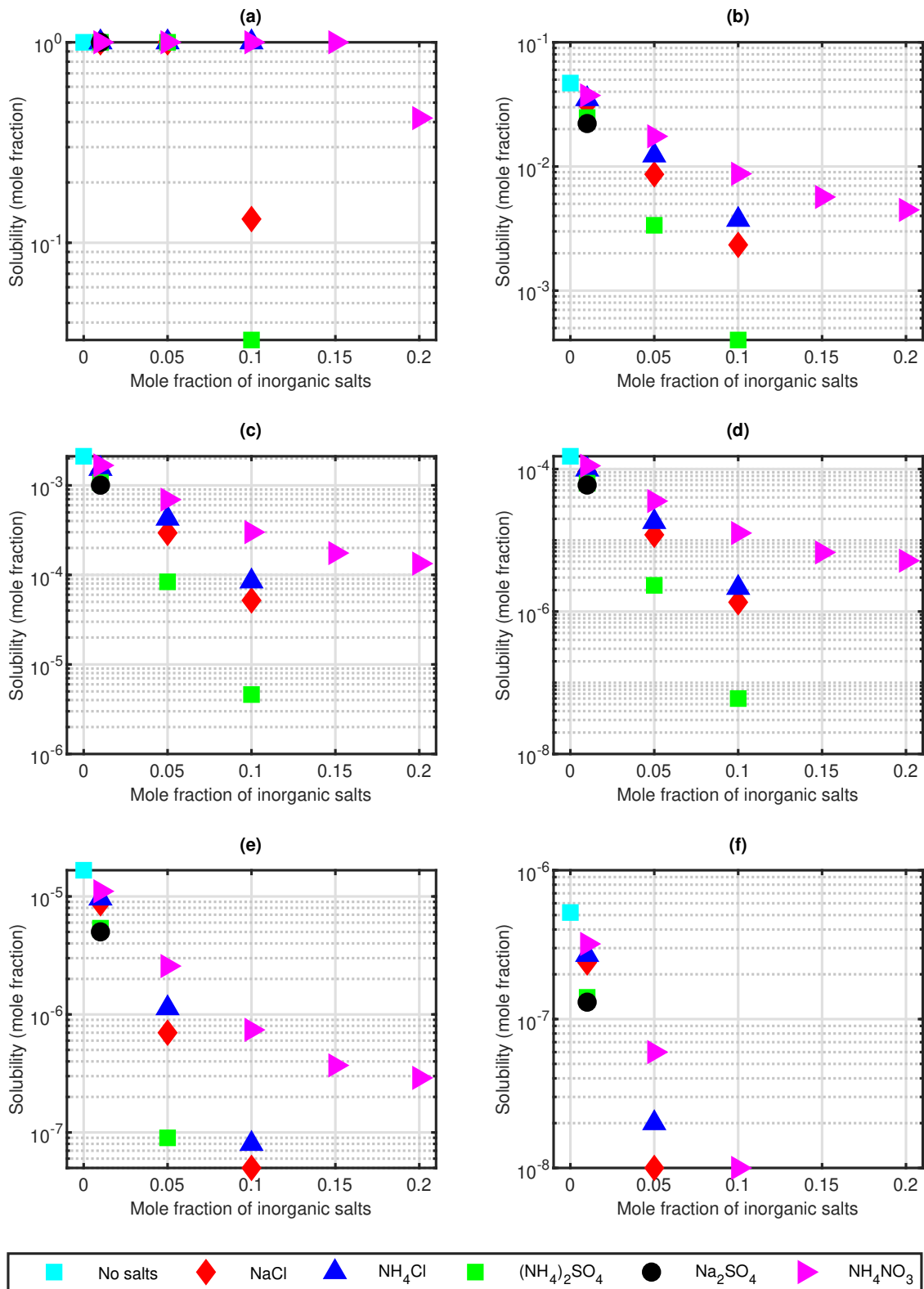
Figure (1) Solubility of a) acetic, b) butanoic, c) hexanoic, d) octanoic e) decanoic and f) dodecanoic acid in neat water and in aqueous solutions with different salt mole fractions, presented on a logarithmic scale.

COSMO*therm* calculates the liquid-liquid and solid-liquid equilibria as the amount of the solute in both the solvent-rich (x_j^{SOL}) and the solute-rich phase $x_j'^{\mathrm{SOL}}$. The solubility of the solvent in the solute-rich phase (here the solubility of the aqueous solvent in the fatty acid) is equal to $1 - x_j'^{\mathrm{SOL}}$. The solubilities of the aqueous solvents (pure water/water–inorganic salt mixtures) in the fatty acids are presented in Figures 2 a-f (the respective values are in Table S2 of the Supporting Information). Similar to the solubilities of the fatty acids in the solvents, the solubilities of the solvents in the fatty acids decrease when the mole fraction of the inorganic salt in the solvent increases. However, the mole fraction based solubilities of the solvent mixtures in the fatty acids are higher than of the fatty acids in the solvent mixtures.
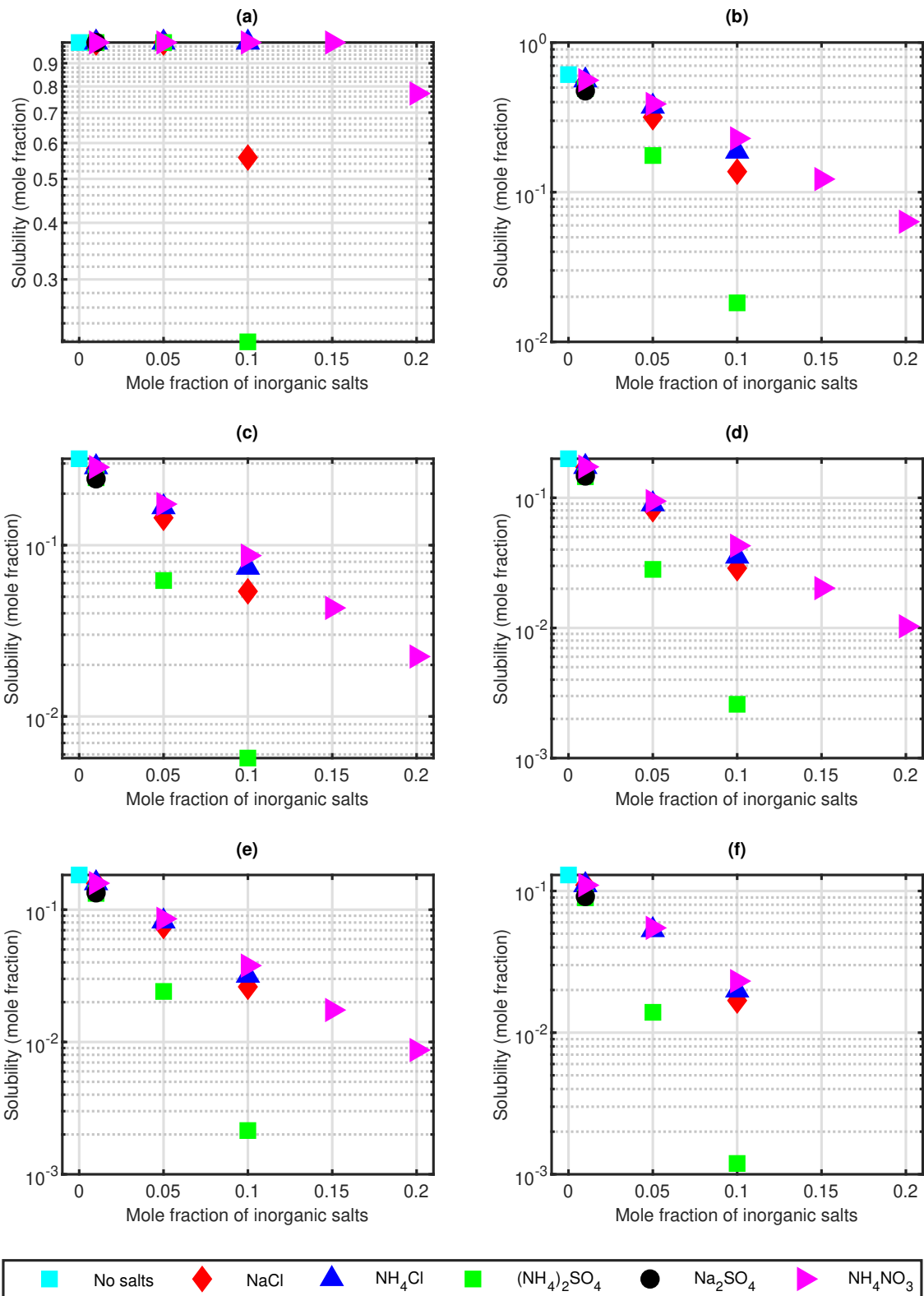
Figure (2)   Solubilities of the studied aqueous solvents in a) acetic, b) butanoic, c) hexanoic, d) octanoic e) decanoic and f) dodecanoic acid, on a logarithmic scale.

21

In Figure 3, we compare the calculated solubilities of the fatty acids in pure water to experimental solubilities measured at 293.15 K.[33,39] The calculated solubilities follow a logarithmic trend with respect to the number of carbon atoms in the acid. COSMO*therm* overestimates the solubilities of hexanoic and octanoic acid compared to the experimental solubilities, while for decanoic and dodecanoic acid, COSMO*therm* predicts lower solubilities compared to the experimental values. The experimental solubilities for acetic and butanoic acid are not shown in the figure as they are fully soluble in water. COSMO*therm* also predicts that acetic acid is infinitely soluble in water while the estimated solubility of butanoic acid in water is $x_{but} = 25.09$g/100g of H_2O. The solubilities of the fatty acids in water were also calculated taking the acid dissociation constant into account. The results did not show any significant difference compared to the values calculated without the pK_a except in case of dodecanoic acid, which has the lowest and most uncertain solubility estimate.
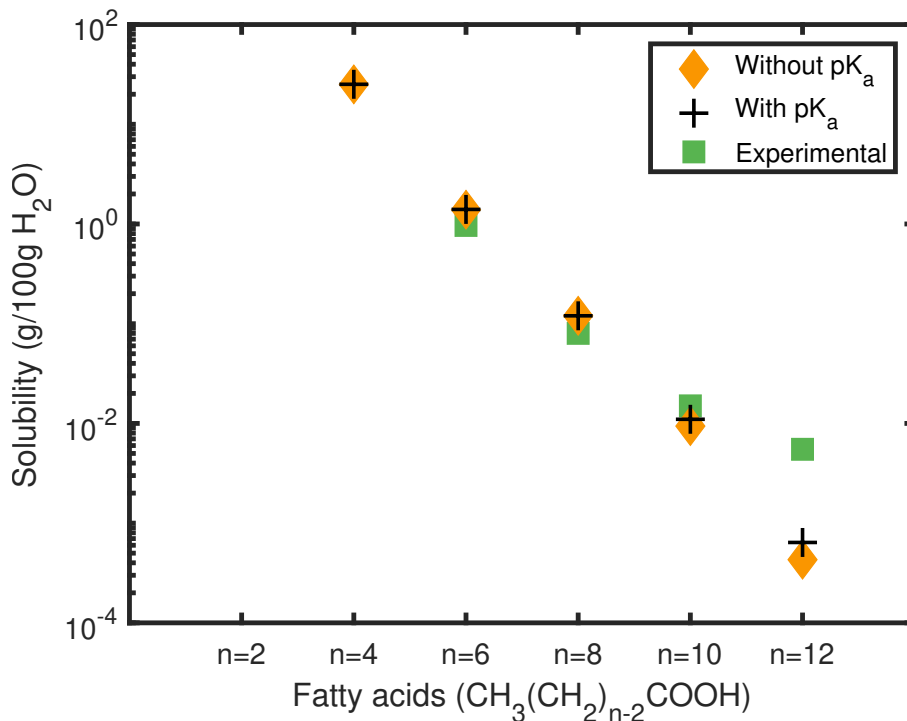
Figure (3)   Experimental and calculated (with and without the pK_a) solubility values of the studied acids in water at 293.15 K, with y-axis on a logarithmic scale.

The computed Setschenow constants (K_s) of acetic, butanoic and hexanoic acids in aque-

ous NaCl solutions were compared to the experimental values of K_s reported by Xie et al.[54] and they are presented in Table 4. The Setschenow constants were expressed in l/mol and for the conversion of the mole fraction of NaCl to molar concentration we used the density of the binary water–NaCl solutions presented also in Table 4.

Table (4) Setschenow constants K_s of acetic, butanoic and hexanoic acid in aqueous solutions with sodium chloride derived from experimental studies and COSMO*therm* calculations and densities ρ of the aqueous solutions of NaCl with 1% and 5% mole fraction of inorganic salt.

Aqueous solution	K_s (exp.) [M^{-1}]	K_s (COSMO) [M^{-1}]		ρ [g/cm^3]	
		NaCl 1%	NaCl 5%	NaCl 1%	NaCl 5%
CH_3COOH - NaCl	0.064 [a]	0	0	-	-
$CH_3(CH_2)_2COOH$ - NaCl	0.166 [a]	0.292	0.258	-	-
$CH_3(CH_2)_4COOH$ - NaCl	0.22 [a]	0.3	0.302	-	-
NaCl	-	-	-	1.0198 [b]	1.1042 [b]

[a] Xie et al. (1985)[54] [b] Rowe et al. (1970)[42]

Figure 4 shows that, COSMO*therm* can correctly predict a salting out effect (positive K_s values) for acetic, butanoic and hexanoic acid when they are dissolved in water with 1% and 5% of mole fraction of NaCl. Compared to the experimental results, COSMO*therm* underestimates the salting out effect for acetic acid, for which the calculated solubility values result in $K_s = 0$, as it was found completely soluble in water and in the solutions with small fractions of NaCl. For all other cases COSMO*therm* overestimates the experimentally determined salting out. Previous studies have also reported overestimation of experimentally predicted salting out effects by COSMO*therm* in aqueous organic–inorganic salt mixtures with sodium chloride[55,56] and ammonium sulfate.[55,57] Toivola et al.[55] attributed this deviation to the overestimation of the molecular interactions in the solution. Here, the K_s of butanoic acid deviates more from the corresponding experimental value. Both computed and experimental values of K_s in Figure 4 show that fatty acids with longer aliphatic chains are salting out more strongly than the fatty acids with shorter carbon chains, which is in agreement with other reported salting effects in solutions of organic compounds (e.g. ketones and alkyl benzenes) with increasing carbon atoms.[56,57] The length of the carbon chain will not

substantially directly affect the polarity of the carboxylic group, and thus the actual specific interactions between the polar head and the water molecules and/or ions. This indicates that the increase/decrease of the volume of the acid can enhance or weaken, respectively, the interactions between the ions of NaCl and the water molecules. Thus, we can expect also for the larger organic fatty acids (C_8–C_{12}) to salt out, but likely to a lesser extent than predicted by COSMO*therm*.
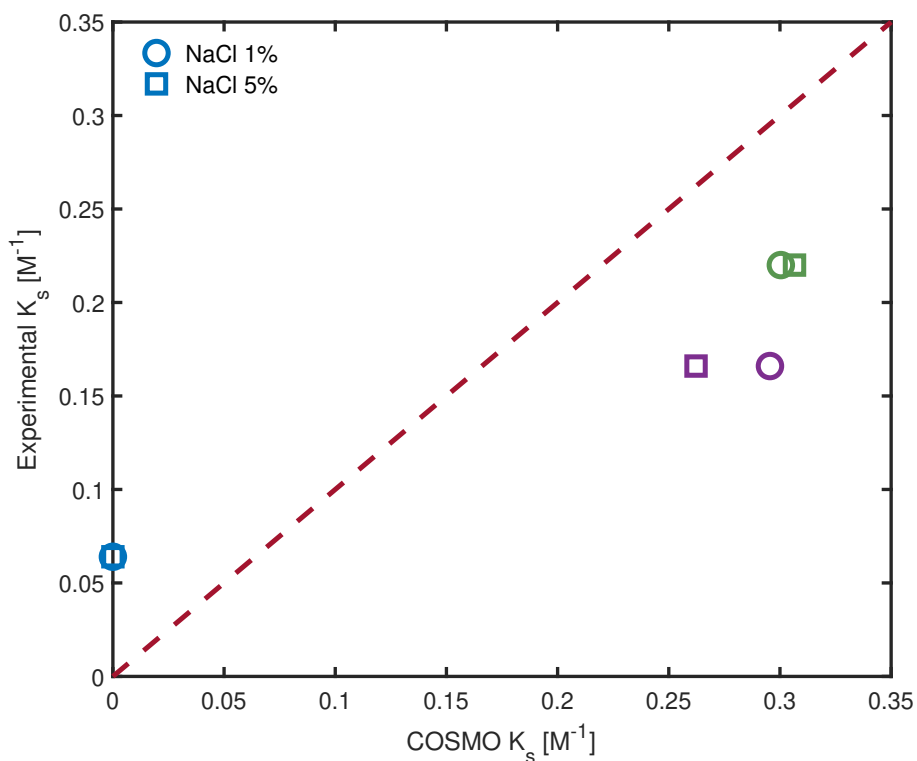

Figure (4)   COSMO*therm* and experimental Setschenow constants of acetic (blue), butanoic (purple) and hexanoic (green) acid in mixed aqueous solutions with different amounts of dissolved NaCl.

Activity coefficients

We calculated the mole fractions based activity coefficients γ of the fatty acids at infinite dilution state in the solvent mixtures with respect to pure component reference state. The calculated activity coefficients are shown in Figures 5 a-f as a function of the inorganic salt mole fraction. The values are also presented in Table S3 of the Supporting Information. In

24

all cases, the γ values are higher than 1, and we observe that when the length of the carbon chain of the fatty acid increases, the ternary systems deviate more strongly from ideality ($\gamma = 1$). The activity coefficients of the fatty acid increases when the mole fraction of the salt in the solvent increases, which is consistent with a salting out effect of the salts. The γ values of the fatty acids are higher for mixtures with polyvalent salt ions (Na_2SO_4 and ($NH_4)_2SO_4$) indicating stronger ion-ion and ion-water interactions. The trend in deviation of activity from ideal solution supports the trend in decreasing solubility of the acids. The computed activity coefficients of the acids have also been plotted as function of the ionic strength of the salt and is presented in Figure S3 of the Supporting Information. The activity coefficient are the lowest in aqueous solutions of NH_4NO_3 compared to the other inorganic salts.
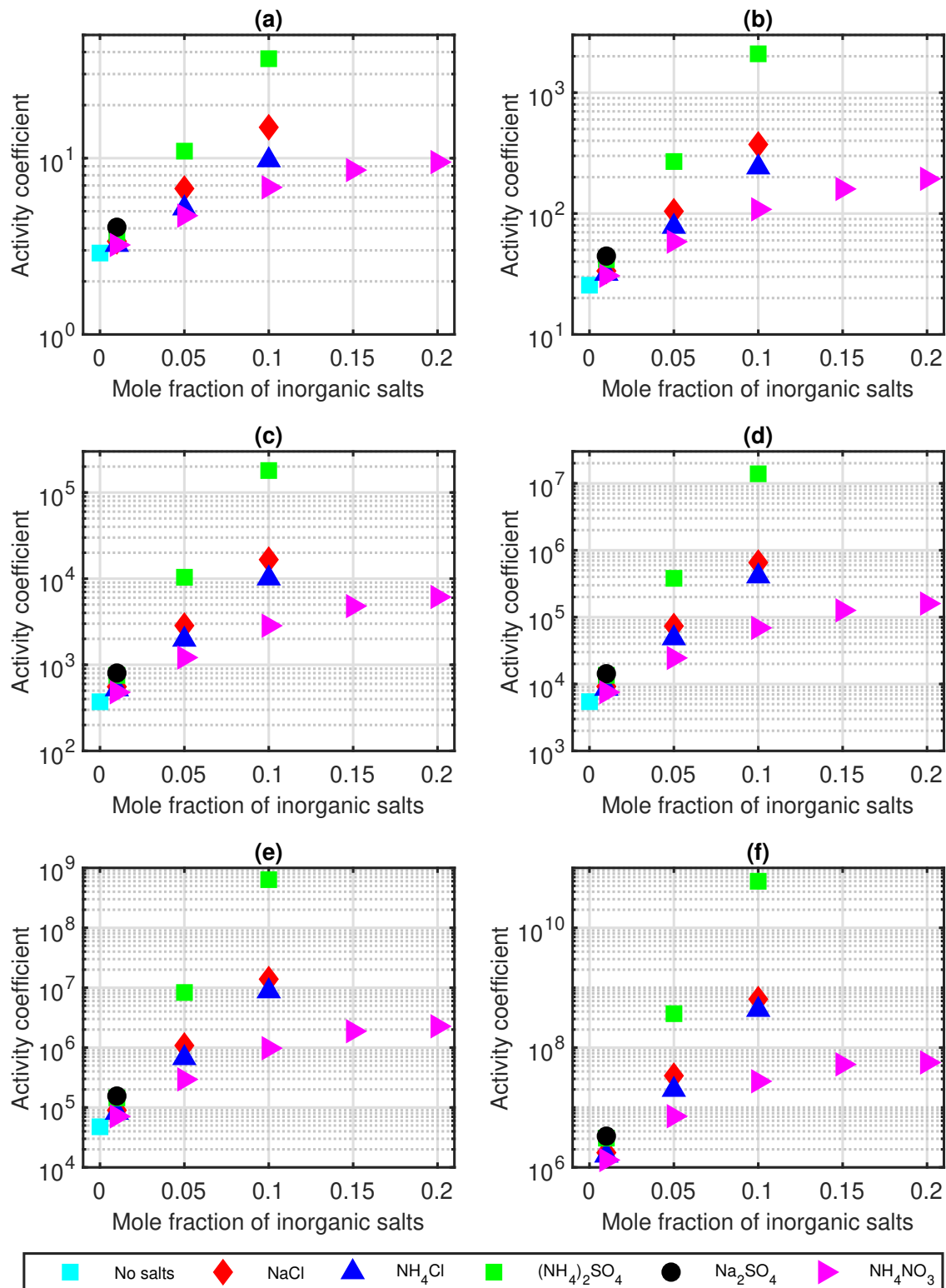
Figure (5)   Activity coefficients of the fatty acids C_2–C_{12}, corresponding to the plots a-f, respectively, at infinite dilution state in aqueous solutions of inorganic salts, at 298.15 K. The values of activity coefficients (y-axis) are on a logarithmic scale.

Fatty acid sodium salts

Solubility

Next we calculated the solubilities of the fatty acid sodium salts. According to solid-liquid equilibrium (SLE) calculations, all of the fatty acid sodium salts are fully miscible with pure water and even with aqueous inorganic salt solutions with high mole fractions of inorganic salt. We therefore calculated the SLE for the ternary systems containing the fatty acid sodium salt and 0.09 mole fraction aqueous solution of inorganic salt. The solubilities of organic sodium salts were calculated using hydrated sodium cations with up to 5 H_2O molecules as the sodium ion of the organic salt. The dependency of the solubility to the number of water molecules is shown in Figure S3. The hydrated Na^+ with 5 H_2O was considered as the best option since in cases with fewer water molecules a salting in effect was observed for small mole fractions.

The relative solubility of fatty acid sodium salts was scaled with respect to the absolute (SLE) solubility of the organic salts in aqueous solutions with 0.09 mole fraction of inorganic salt.

The results are presented in Figure 6. In case of solutions with $(NH_4)_2SO_4$, COSMO*therm* could calculate the absolute solubility of all the organic salts mixed with water and 0.09 mole fraction of inorganic salt and thus we were able to estimate the solubility of the organic salts for all the solutions containing $(NH_4)_2SO_4$. For all the mole fractions of $(NH_4)_2SO_4$ in the solvent, we observe a salting out effect which is more pronounced as the mole fraction of the inorganic salt increases.
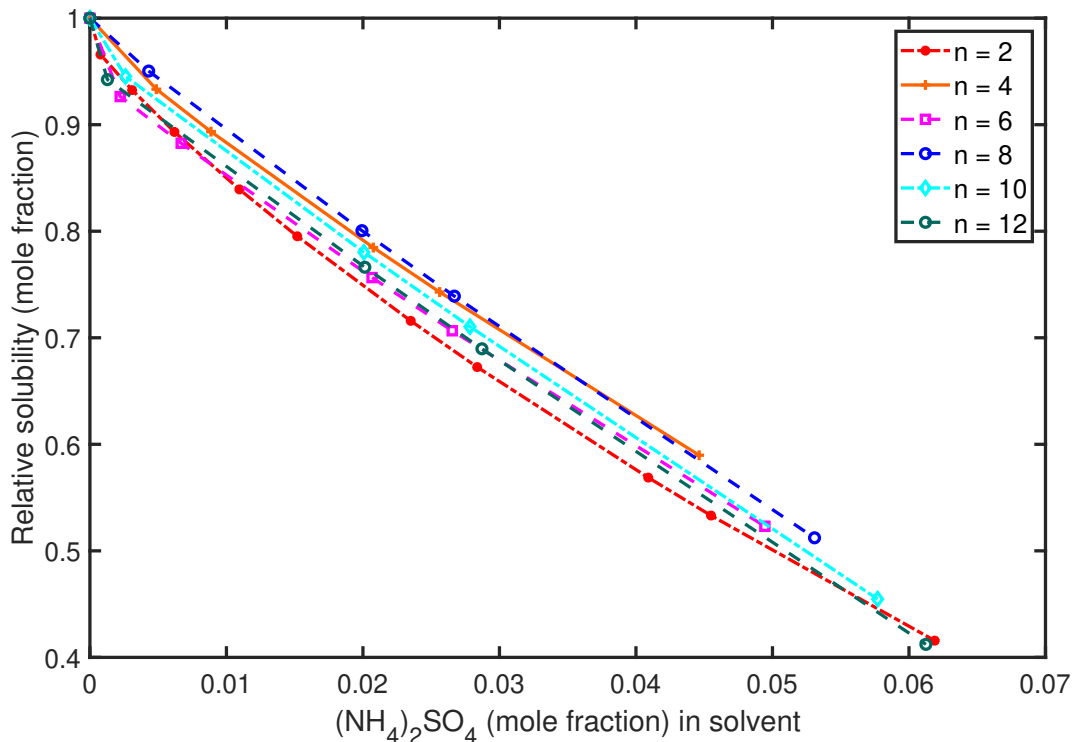
Figure (6) Relative solubility of C_2–C_{12} fatty acid sodium salts $(CH_3(CH_2)_{n-2}COONa)$ in mixtures with water and $(NH_4)_2SO_4$. In each case, the sodium of the organic salt was hydrated with 5 water molecules.

In Figures 7 a-b we present the relative solubility of sodium decanoate and sodium do-decanoate in three different solvent systems: water–$(NH_4)_2SO_4$, water–NH_4NO_3 and water–NH_4Cl. For solutions with $(NH_4)_2SO_4$ and NH_4Cl we observe a steady salting out effect with increasing inorganic salt fraction but in case of NH_4NO_3 COSMO*therm* predicts a sig-nificant salting in effect for both sodium decanoate and sodium dodecanoate. The salting-in effect on sodium decanoate in ternary solutions with NH_4NO_3 increases continually with increasing mole fraction of the inorganic salt. For sodium dodecanoate the effect peaks at small mole fractions of the inorganic salt and decreases moderately for higher mole fractions. This behavior is similar to what we observed for solutions with $(NH_4)_2SO_4$ when less than five water molecules were in the hydrated Na^+ and we therefore suspect it can be related to poor estimation of molecular interactions from COSMO*therm*, rather than a physical phenomenon.
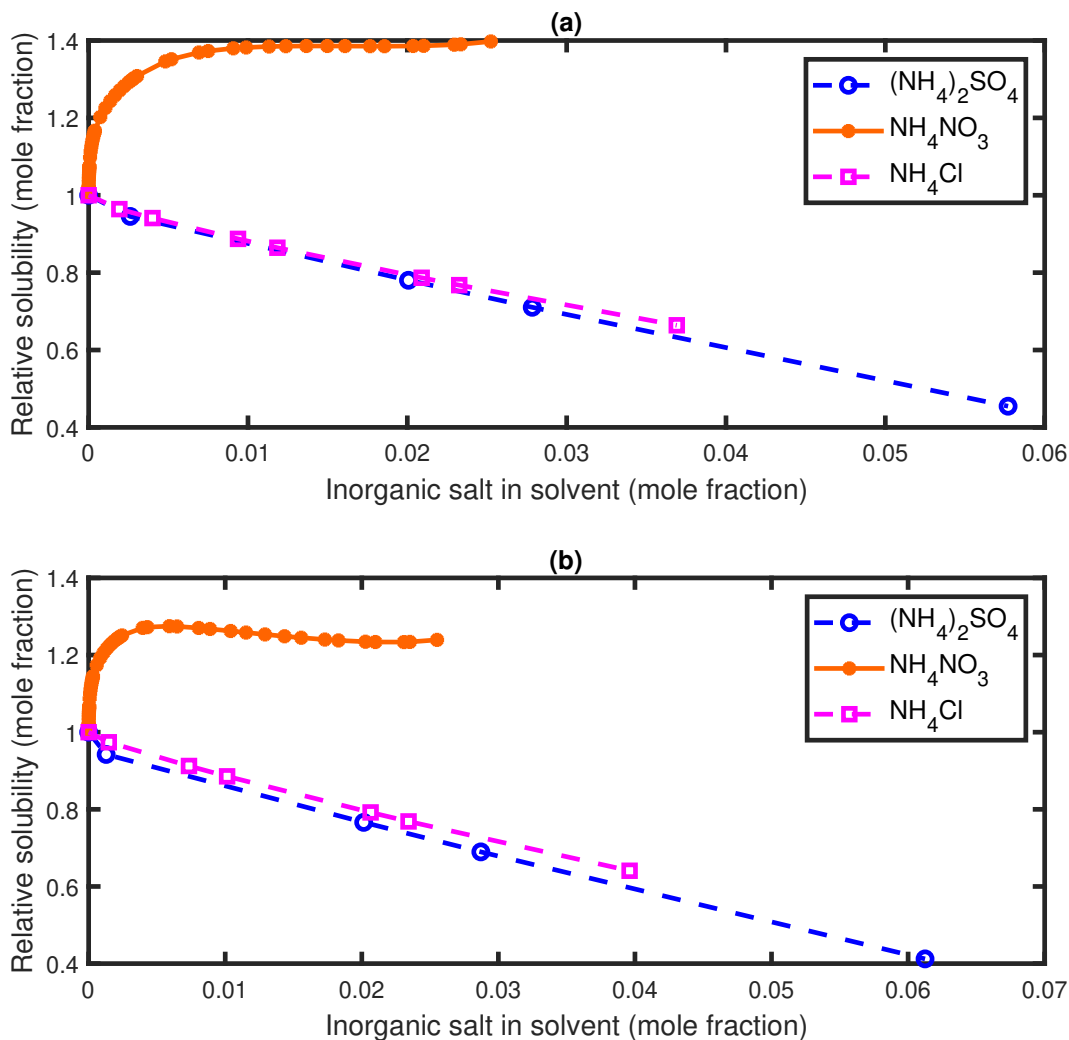
Figure (7) Relative solubility of a) sodium decanoate and b) sodium dodecanoate, when in ternary (water–inorganic salt) solutions. The reference solubility is that of the binary system fatty acid sodium salt–water.

Mean ionic activity coefficients

The calculated mean ionic activity coefficients of the fatty acid sodium salts at the infinite dilution of the solvents are presented in Figures 8 a-f. We observe that the mean activity coefficients are lower than 1 (ideal behaviour) in all cases. The values of binary aqueous solutions are the highest (closer to ideal behaviour) and increasing of the mole fraction of the inorganic salt leads to the decrease of the mean ionic activity coefficients with respect to the binary solution. The only exceptions are solutions of sodium octanoate, sodium

decanoate and sodium dodecanoate with 0.1 mole fraction of $(NH_4)_2SO_4$, where the mean ionic activity coefficient is higher compared to the above-mentioned solutions with lower mole fraction of the inorganic salt. The results of mean ionic activity coefficients contradict the results from the solubility calculations, where we observed a salting out effect. Note here that as the solute is an electrolyte, it is considered in COSMO*therm* as a separate anion and cation in the solution as opposed to a single entity, like neutral fatty acids. This approach increases the complexity of the intermolecular interactions as all of the ions interact with both the water molecules but also with each other. The interactions are now stronger than in the case of acids, since Coulomb (and not dispersion) forces dominate. The mean ionic activity coefficients were calculated without solvating the sodium cation of the fatty acid salt and the results show that COSMO*therm* overpredicts these interactions, and cannot capture the salting out effect.

We also observe a clear dependence of the alkyl chain length of the fatty acid salts on the mean activity coefficient. The charge density of the fatty acid salt in the solution decreases as its molecular size increases and that results in weaker solute–solvent interactions. The values of the mean activity coefficients are presented in Table S5 of the Supporting Information.
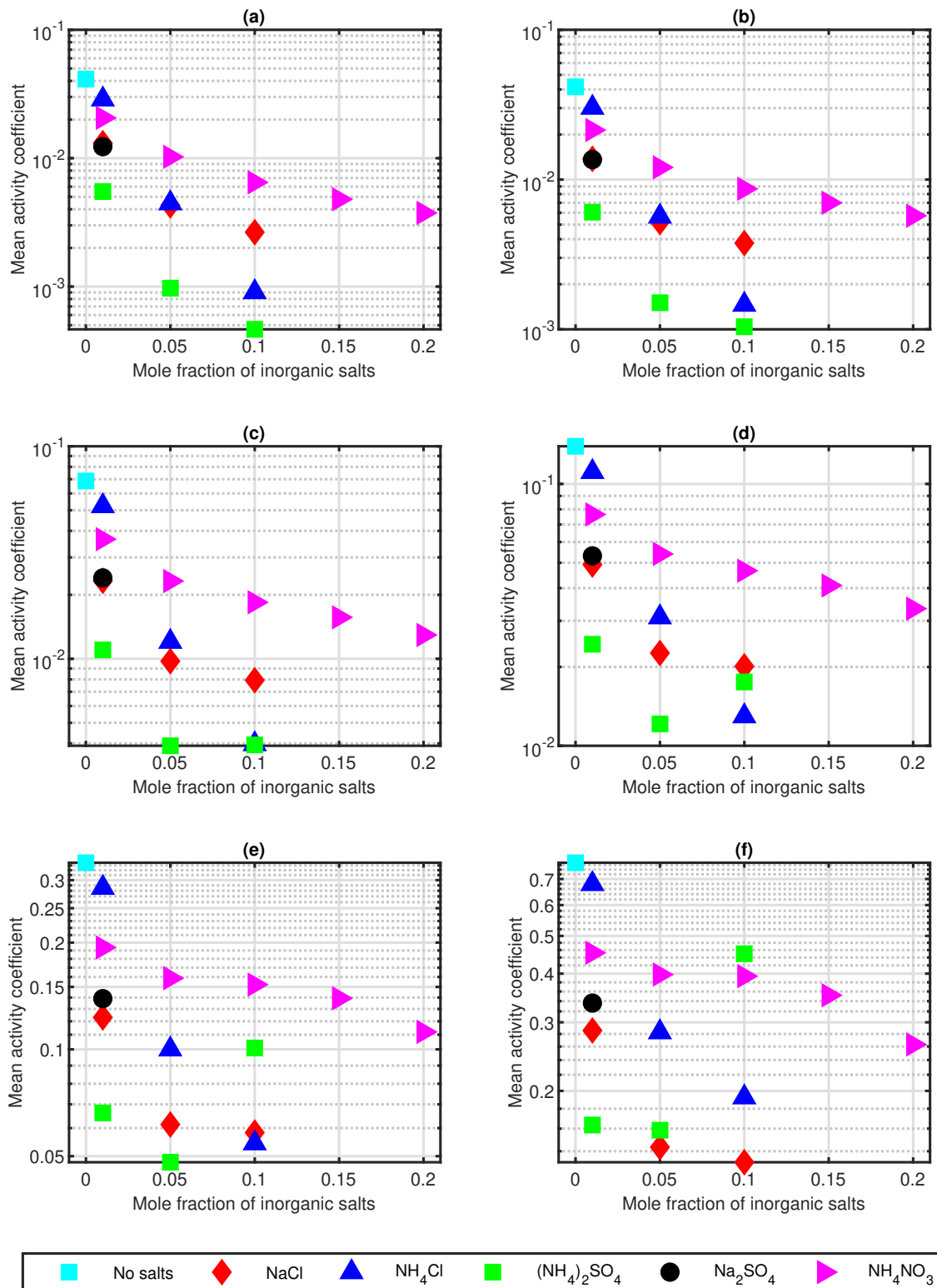
Figure (8)   Calculated mean ionic activity coefficients of a) sodium acetate, b) sodium butanoate, c) sodium hexanoate, d) sodium octanoate, e) sodium decanoate and f) sodium dodecanoate in aqueous mixtures with inorganic salts. The x-axis is linear while the y-axis is on logarithmic scale.

The mean ionic activity coefficients of sodium decanoate in aqueous sodium decanote mixtures were also calculated with infinite dilution reference state (asymmetric convention) for the compositions studied by De Lisi et al.[51] and Sharma et al.[52] The comparison of the calculated mean activity coefficients of sodium decanoate in water from COSMO*therm* and the experimentally derived values are presented in Figure 9. According to Debye-Hückel theory the mean ionic activity coefficient at infinite dilution of sodium decanoate is 1. For very small fractions of the organic salt, the calculated values by COSMO*therm* are lower than these that were derived experimentally, while after 0.005 mole fraction of sodium decanoate there is a better correlation between the two. We observe though that in the binary solutions, the mean ionic activity coefficients are close to the experimental values, which shows that COSMO*therm* estimates better the $\gamma_\pm$ values for the binary solutions compared to the ternary.
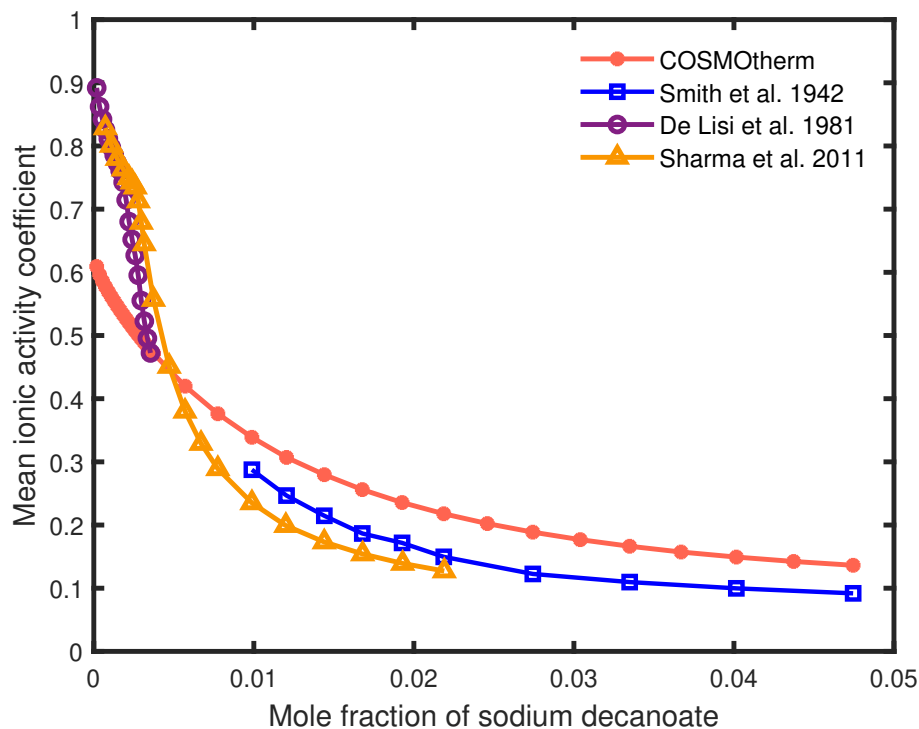

Figure (9) Comparison of COSMO*therm* and experimentally derived mean activity coefficients of sodium decanoate.

The computed mean activity coefficients of the C_2–C_8 fatty acid sodium salts were com-

pared with the reported values in the experimental study of Smith et al.[50] and the results are presented in Figure 10. We observe that for the smaller organic salts (C_2–C_6) there is no good agreement between the compared values, while the agreement is better in the case of sodium octanoate. This can be related to overestimation of the surface charge density of small ions by COSMO*therm* which leads to overestimated intermolecular interactions with the solvent molecules.
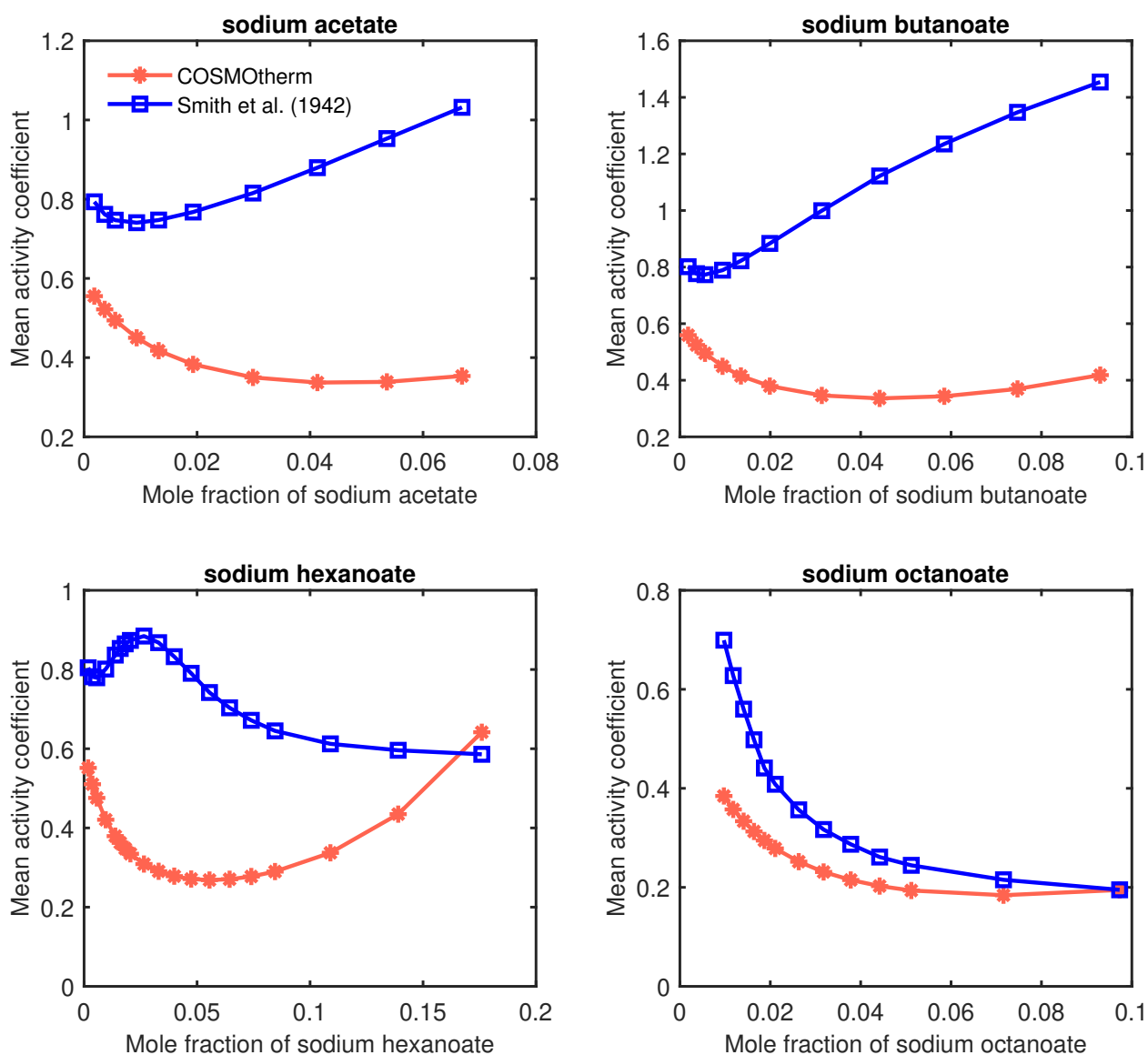

Figure (10) Calculated mean activity coefficients of C_2–C_8 fatty acid sodium salts ($CH_3(CH_2)_{n-2}COONa$) in aqueous mixtures and comparison with the values given by Smith et al.[50]

The contribution of surfactants to cloud formation by organic aerosol can be estimated from the critical saturation ratio of a droplet solution using Köhler theory, which takes into account the activity of water in solution and the surface tension of the droplet. In an aqueous solution, increase of the organic activity coefficient can decrease the solubility of the organic compound and promote surface partitioning of surfactants. Activity coefficients of complex systems are exceedingly difficult to determine experimentally. Most droplet activation and cloud microphysics models therefore assume ideal activities equal to the mole fraction concentration of the component. In case of surfactants, these approximations can lead to underestimation of the bulk–surface partitioning (ratio of the concentration of the surfactant in the bulk to the concentration of the surfactant in the surface) and thereby to overestimation of the surface tension of the droplet.[18,19] Both effects would bias prediction of cloud droplet activation towards lower critical saturation ratios and larger activated droplets.[19]

Conclusions

We used COSMO*therm* to calculate the solubility and activity coefficients of even C_2–C_{12} fatty acids and their sodium salts in binary aqueous and mixed aqueous–inorganic salt solvents. Fatty acids are major components of organic aerosol fractions and have atmospheric relevance as they alter the water phase equilibrium of rain drops, cloud droplets, and cloud condensation nuclei (CCN).

We found a good agreement between the estimated and experimental solubilities of binary aqueous solutions of the fatty acids, with COSMO*therm* giving slightly lower solubility values for organic acids with longer aliphatic chains (decanoic and dodecanoic acid) compared to experiments. For ternary systems containing water, a fatty acid and an inorganic salt (NaCl, NH_4Cl, $(NH_4)_2SO_4$, Na_2SO_4 and NH_4NO_3), we observed a salting out effect. In aqueous solutions of acetic, butanoic and hexanoic acid with NaCl, the comparison between

the computed and experimentally observed Setschenow constants show that COSMO*therm* correctly predicts the existence of a salting out effect, but tends to overestimate its magnitude (butanoic and hexanoic acid), in agreement with the studies of Toivola et al.[55] and Wang et al.[57] We observed an enhancement of the salting out effect with increase of the aliphatic chain length of the fatty acid.

The fatty acid sodium salts were found miscible in both pure water and aqueous–inorganic salt mixtures. However, the computed relative solubilities of the fatty acid sodium salts in the ternary mixtures were lower than in water in all cases, again revealing a salting out effect. In addition, we observed that the interactions in ionic solutions can be better estimated by COSMO*therm* when the sodium cation of the organic salt is surrounded by 5 water molecules.

The calculated activity coefficients of the fatty acids in water and water–salt solutions show positive deviation of the solutions from ideality. This deviation becomes more pronounced with increasing mole fraction of the inorganic salt in the solvent mixture, and with increasing alkyl chain length of the organic compound. The computed mean ionic activity coefficients of the binary water–fatty acid salt systems were in good agreement with experimentally determined values for the larger organic salts (sodium octanoate and sodium decanoate), indicating that COSMO*therm* may overpredict the intermolecular interactions in solutions with smaller solute molecules. The addition of inorganic salts in the activity coefficient calculations resulted in a salting-in effect, as opposed to the results on solubility. This is attributed to overestimation of the long-range intermolecular interactions by COSMO*therm* when the sodium of the fatty acid salt is not hydrated.

The calculated activity coefficients of acids suggest that the common assumption of ideal droplet solutions in cloud microphysics could lead to overestimating the cloud condensation nucleus (CCN) activity of surface active organic aerosol. Our results show that COSMO*therm* could provide a viable route to obtain experimentally inaccessible activity data for organic aerosol components. This would enable more accurate considerations of surfactant effects to be taken into account in cloud microphysics and atmospheric models.

Supporting Information Available

Table S1: Solubilities of fatty acids, Table S2: Solubilities of the solvents in fatty acids, Table S3: Activity coefficients of the fatty acids, Table S4: Ionic strength of the inorganic salts in the studied aqueous solutions, Table S5: Mean activity coefficients of organic salts in the studied solvent mixtures, Figure S1: Solubilities of the fatty acids as a function of ionic strength and concentration of inorganic salts, Figure S2: Activity coefficients of the fatty acids as a function of ionic strength and concentration of inorganic salt, Figure S3: Relative solubility of sodium acetate in water–$(NH_4)_2SO_4$ solvent mixture with different number of water molecules in the Na^+ cation. Equation for the calculation of density of binary water–sodium chloride solutions. (PDF)

.cosmo and .energy files (ZIP)

References

(1) Boucher, O.; Randall, D.; Artaxo, P.; Bretherton, C.; Feingold, G.; Forster, P.; Kerminen, V.-M.; Kondo, Y.; Liao, H.; Lohmann, U. et al. In *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment*

Report of the Intergovernmental Panel on Climate Change; Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Doschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M., Eds.; Cambridge University Press: Cambridge, UK, 2013; pp 571–657.

(2) Zhang, Q.; Jimenez, J. L.; Canagaratna, M.; Allan, J.; Coe, H.; Ulbrich, I.; Alfarra, M.; Takami, A.; Middlebrook, A.; Sun, Y. et al. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere mid-latitudes. *Geophys. Res. Lett.* **2007**, *34*.

(3) Saxena, P.; Hildemann, L. Water-Soluble Organics in Atmospheric Particles: A Critical Review of the Literature and Application of Thermodynamics to Identify Candidate Compounds. *J. Atmos. Chem.* **1996**, *24*, 57–109.

(4) Roberts, G. C.; Andreae, M. O.; Zhou, J.; Artaxo, P. Cloud condensation nuclei in the Amazon Basin:"Marine" conditions over a continent? *Geophys. Res. Lett.* **2001**, *28*, 2807–2810.

(5) Yassaa, N.; Meklati, B. Y.; Cecinato, A.; Marino, F. Particulate n-alkanes, n-alkanoic acids and polycyclic aromatic hydrocarbons in the atmosphere of Algiers City Area. *Atmos. Environ.* **2001**, *35*, 1843–1851.

(6) Liu, X.; Meng, J.; Hou, Z.; Yan, L.; Wang, G.; Yi, Y.; Wei, B.; Fu, M.; Li, J.; Cao, J. Molecular Compositions and Sources of Organic Aerosols from Urban Atmosphere in the North China Plain during the Wintertime of 2017. *Aerosol Air Qual. Res.* **2019**, *19*, 2267–2280.

(7) Graham, B.; Guyon, P.; Taylor, P. E.; Artaxo, P.; Maenhaut, W.; Glovsky, M. M.; Flagan, R. C.; Andreae, M. O. Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography-mass spectrometry. *J. Geophys. Res.* **2003**, *108(D24)*, 4766.

(8) Li, Y. C.; Yu, J. Z. Simultaneous determination of mono- and dicarboxylic acids, omega-oxo-carboxylic acids, midchain ketocarboxylic acids, and aldehydes in atmospheric aerosol samples. *Environ. Sci. Technol.* **2005**, *39*, 7616–7624.

(9) Zhao, Y.; Ren, H.; Deng, J.; Li, L.; Hu, W.; Ren, L.; Yue, S.; Fan, Y.; Wu, L.; Li, J. et al. High daytime abundance of primary organic aerosols over Mt. Emei, Southwest China in summer. *Sci. Total Environ.* **2019**, 134475.

(10) Mochida, M.; Kawamura, K.; Umemoto, N.; Kobayashi, M.; Matsunaga, S.; Lim, H.-J.; Turpin, B.; Bates, T.; Simoneit, B. Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign. *J. Geophys. Res.* **2003**, *108*, D23S8638.

(11) Mochida, M.; Umemoto, K., N.and Kawamura; Lim, H. J.; Turpin, B. J. Bimodal size distributions of various organic acids and fatty acids in the marine atmosphere: Influence of anthropogenic aerosols, Asian dusts, and sea spray off the coast of East Asia. *J. Geophys. Res.: Atmos.* **2007**, *112*, D15209.

(12) Barger, W. R.; Garrett, W. D. Surface active organic material in the marine atmosphere. *J. Geophys. Res.* **1970**, *75*, 4561–4566.

(13) Mochida, M.; Kitamori, Y.; Kawamura, K.; Nojiri, Y.; Suzuki, K. Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt particles. *J. Geophys. Res.* **2002**, *107*, D17S4325.

(14) Cheng, Y.; Li, S.-M.; Leithead, A.; Brickell, P. C.; Leaitch, W. R. Characterizations of *cis*-pinonic acid and n-fatty acids on fine aerosols in the Lower Fraser Valley during Pacific 2001 Air Quality Study. *Atmos. Environ.* **2004**, *38*, 5789–5800.

(15) Quinn, J.; Wade, T. Lipid measurements in the marine atmosphere and the sea surface microlayer. *Baseline Studies of Pollutants in the Marine Environment* **1972**, 633–663.

(16) Campbell, A. N.; Lakshminarayanan, G. R. Conductances and Surface Tensions of Aqueous Solutions of Sodium Decanoate Sodium Laurate and Sodium Myristate at 25 °C and 35 °C. *Can. J. Chem.* **1965**, *43*, 1729–1737.

(17) Fainerman, V. B.; Miller, R.; Möhwald, H. General Relationships of the Adsorption Behavior of Surfactants at the Water/Air Interface. *J. Phys. Chem. B* **2002**, *106*, 809–819.

(18) Prisle, N. L.; Raatikainen, T.; Sorjamaa, R.; Svenningsson, B.; Laaksonen, A.; Bilde, M. Surfactant partitioning in cloud droplet activation: a study of C8, C10, C12 and C14 normal fatty acid sodium salts. *Tellus* **2008**, *60B*, 416–431.

(19) Prisle, N. L.; Raatikainen, T.; Laaksonen, A.; Bilde, M. Surfactants in cloud droplet activation: mixed organic-inorganic particles. *Atmos. Chem. Phys.* **2010**, *10*, 5663–5683.

(20) Prisle, N. L.; Dal Maso, M.; Kokkola, H. A simple representation of surface active organic aerosol in cloud droplet formation. *Atmos. Chem. Phys.* **2011**, *11*, 4073–4083.

(21) Forestieri, S. D.; Staudt, S. M.; Kuborn, T. M.; Faber, K.; Ruehl, C. R.; Bertram, T. H.; Cappa, C. D. Establishing the impact of model surfactants on cloud condensation nuclei activity of sea spray aerosol mimics. *Atmos. Chem. Phys.* **2018**, *18*, 10985–11005.

(22) Petters, S. S.; Petters, M. D. Surfactant effect on cloud condensation nuclei for two-component internally mixed aerosols. *J. Geophys. Res.: Atmos.* **2016**, *121*, 1878–1895.

(23) Prisle, N.; Lin, J.; Purdue, S.; Lin, H.; Meredith, J.; Nenes, A. Cloud condensation nuclei activity of six pollenkitts and the influence of their surface activity. *Atmos. Chem. Phys.* **2019**, *19*, 4741–4761.

(24) Facchini, M.; Decesari, S.; Mircea, M.; Fuzzi, S.; Loglio, G. Surface Tension of At-

mospheric Wet Aerosol and Cloud/Fog Droplets in Relation to their Organic Carbon Content and Chemical Composition. *Atmos. Environ.* **2000**, *34*, 4853–4857.

(25) Köhler, H. The Nucleus in and the Growth of Hygroscopic Droplets. *Trans. Faraday Soc.* **1936**, *32*, 1152–1161.

(26) Gill, P. S.; Graedel, T. E.; Weschler, C. J. Organic Films on Atmospheric Aerosol-Particles, Fog Droplets, Cloud Droplets, Raindrops, and Snowflakes. *Rev. Geophys. Space Phys.* **1983**, *21*, 903–920.

(27) Lin, B.; McCormick, A. V.; Davis, H. T.; Strey, R. Solubility of sodium soaps in aqueous salt solutions. *J. Colloid Interface Sci.* **2005**, *291*, 543–549.

(28) Kurtén, T.; Elm, J.; Prisle, N. L.; Mikkelsen, K. V.; Kampf, C. J.; Waxman, E. M.; Volkamer, R. Computational Study of the Effect of Glyoxal–Sulfate Clustering on the Henry's Law Coefficient of Glyoxal. *J. Phys. Chem. A* **2014**, *119*, 4509–4514.

(29) COSMO*therm*, version C3.0, Release 19, COSMO*logic* GmbH & Co. KG., Leverkusen, Germany. 2019.

(30) Kurtén, T.; Hyttinen, N.; D'Ambro, E. L.; Thornton, J.; Prisle, N. L. Estimating the saturation vapor pressures of isoprene oxidation products $C_5H_{12}O_6$ and $C_5H_{10}O_6$ using COSMO-RS. *Atmos. Chem. Phys.* **2018**, *18*, 17589–17600.

(31) Spartan'14, Wavefunction Inc., Irvine, CA. 2014.

(32) COSMO*conf*, 4.1, COSMO*logic* GmbH & Co KG. 2019; `http://www.cosmologic.de`.

(33) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 85th ed.; CRC Press LLC, 2004.

(34) Arpe, H.; Pikart-Müller, M.; Ullmann, F. *Ullmann's encyclopedia of industrial chemistry. Index : A 1 to A 24, B 1 to B 4. (Abrasives to stains, microscopic, fundamentals of chemical engineering, unit operations I and II, and principles of chemical reaction engineering and plant design)*; VCH-Verlag-Ges., 1994.

(35) Ferloni, P.; Sanesi, M.; Franzosini, P. Phase Transitions in the Alkali C1 —n. C4 Alkanoates. *Z. Naturforsch. A* **1975**, *30*, 1447–1457.

(36) Duruz, J. J.; Michels, H. J.; Ubbelohde, A. R. J. P. Molten fatty acid salts as model ionic liquids. I. Thermodynamic and transport parameters of some organic sodium salts. *Proc. R. Soc. London, Ser. A* **1971**, *322*, 281–299.

(37) Michels, H. J.; Ubbelohde, A. R. Melting mechanisms of n-alkanecarboxylates ($C_nH_{2n+1}CO_2^-$; n ≤ 6). *J. Chem. Soc., Perkin Trans. 2* **1972**, 1879–1881.

(38) Zacharie, B.; Ezzitouni, A.; Duceppe, J.-S.; Penney, C. A Simple and Efficient Large-Scale Synthesis of Metal Salts of Medium-Chain Fatty Acids. *Org. Process Res. Dev.* **2009**, *13*, 581–583.

(39) Perry, R.; Green, D.; Maloney, J. *Perry's Chemical Engineers' Handbook*; International student edition; McGraw-Hill, 1997.

(40) Barratt, M.; Dixit, M.; Jones, P. The use of in vitro cytotoxicity measurements in QSAR methods for the prediction of the skin corrosivity potential of acids. *Toxicol. in Vitro* **1996**, *10*, 283 – 290.

(41) Serjeant, E. P.; Dempsey, B. *Ionisation constants of organic acids in aqueous solution*, 1st ed.; Pergamon Press, Oxford, 1979.

(42) Rowe, A. M. J. Pressure-volume-temperature-concentration relation of aqueous NaCl solutions. *J. Chem. Eng. Data* **1970**, *15*, 61–66.

(43) Toure, O.; Audonnet, F.; Lebert, A.; Dussap, C.-G. COSMO-RS-PDHS: A new predictive model for aqueous electrolytes solutions. *Chem. Eng. Res. Des.* **2014**, *92*, 2873 – 2883.

(44) Toure, O.; Audonnet, F.; Lebert, A.; Dussap, C.-G. Development of a thermodynamic model of aqueous solution suited for foods and biological media. Part A: Prediction of

activity coefficients in aqueous mixtures containing electrolytes. *Can. J. Chem. Eng.* **2015**, *93*, 443–450.

(45) Levine, I. N. *Physical Chemistry*, 6th ed.; McGraw-Hill: New York, USA, 2009; pp 295–302.

(46) Van Ness, H. C.; Abbott, M. M. Vapor-liquid equilibrium. Part VI. Standard state fugacities for supercritical components. *AIChE J.* **1979**, *25*, 645–653.

(47) Prausnitz, J.; Lichtenthaler, R.; de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall PTR, 1999.

(48) Soustelle, M. *Chemical Equilibria*; John Wiley & Sons: Hoboken, NJ, USA, 2015; p 210.

(49) Honig, J. M. *Thermodynamics : Principles Characterizing Physical and Chemical Processes*; Elsevier/Academic Press, 2007; p 452.

(50) Smith, E. R.; Robinson, R. The vapour pressures and osmotic coefficients of solutions of the sodium salts of a series of fatty acids at 25°. *Trans. Faraday Soc.* **1942**, *38*, 70–78.

(51) De Lisi, R.; Perron, G.; Paquette, J.; Desnoyers, J. E. Thermodynamics of micellar systems: activity and entropy of sodium decanoate and n-alkylamine hydrobromides in water. *Can. J. Chem.* **1981**, *59*, 1865–1871.

(52) Sharma, P.; MacNeil, J. A.; Bowles, J.; Leaist, D. G. The unusual importance of activity coefficients for micelle solutions illustrated by an osmometry study of aqueous sodium decanoate and aqueous sodium decanoate+ sodium chloride solutions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21333–21343.

(53) Wang, C.; Lei, Y. D.; Wania, F. Effect of Sodium Sulfate, Ammonium Chloride, Ammonium Nitrate, and Salt Mixtures on Aqueous Phase Partitioning of Organic Compounds. *Environ. Sci. Technol.* **2016**, *50*, 12742–12749.

(54) Xie, W.; Ji, H.; Li, W. The calculation method of a modified equation of the internal pressure salt effect theory. *Acta Physico-Chimica Sinca* **1985**, *1*, 304–307.

(55) Toivola, M.; Prisle, N. L.; Elm, J.; Waxman, E. M.; Volkamer, R.; Kurtén, T. Can COSMOTherm Predict a Salting in Effect? *J. Phys. Chem. A* **2017**, *121*, 6288–6295.

(56) Endo, S.; Pfennigsdorff, A.; Goss, K.-U. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. *Environ. Sci. Technol.* **2012**, *46*, 1496–1503.

(57) Wang, C.; Lei, Y. D.; Endo, S.; Wania, F. Measuring and Modeling the Salting-out Effect in Ammonium Sulfate Solutions. *Environ. Sci. Technol.* **2014**, *48*, 13238–13245.

Graphical TOC Entry