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Supporting information for: Model for estimating activity coefficients in binary and ternary ionic surfactant solutions

The CMC based ionic surfactant activity model (CISA) for atmospheric applications

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1 Thermodynamics of aqueous electrolyte solutions

Electrolytic compounds dissociate when dissolved in polar solvents modifying the relative proportions of solvent and solute in solution. Due to the ion–ion and ion–solvent interactions, the properties of electrolyte solutions deviate more from the ideal solution model than solutions of neutral molecules at equivalent concentrations. The thermodynamic variable that accounts for these deviations is the activity coefficient, which is given as the ratio between the activities of i in the solution and the equivalent ideal solution of the same concentration $\gamma_i = a_i/a_i^{id}$. Here, both a_i values depend on the concentration scale chosen. Since the density of the electrolyte solutions changes with the concentration, the preferred unit for the solution concentration is the molality m.

The activity also reflects the changes in the cohesive forces experienced by species i in the solution but with respect to the cohesive forces in a reference state. Thus, the calculation of γ_i and a_i requires to define a reference state. This is not easy for solutions of electrolytes because the deviations from the ideal behaviour occur even at very low concentrations. The thermodynamic convention typically assumed is a hypothetical solution of 1 mol kg^{-1} where the solvent behaves as in pure state and the electrolyte behaves ideally, both showing activity coefficients equal to the unity. This asymmetric convention is the so called convention III (Levine, 2008; Soustelle, 2015).

If we consider an aqueous solution that contains 1 kg of water that represents $s \equiv 1/\left(18.0153 \times 10^{-3}\right)$ moles and m_i moles of the dissociating species i where $i =$

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$2 \ldots d$ different salts, we can relate the values of γ_i and a_i to the total Gibbs free energy of the system G in terms of the total number of moles n in solution as

$$\sum_{i=1} n_i \bar{G}_i = s\mu_1 + \sum_{i>1} m_i \mu_i = s\left(\mu_1^o + RT \ln a_1\right) + \sum_{i>1} m_i \left(\mu_i^o + RT \ln a_i\right), \tag{S1}$$

where n_i and μ_i^o are the total number of moles in the solution and the chemical potential in the reference state of the species i. The properties of water are identified with the subscript $i = 1$.

Any model used to calculate γ_i and a_i must be based on a descriptive function for $G = f(m_i)$ as function of the solution composition. Expressions for the activity coefficients are obtained by derivation of this function since $\mu_i \equiv (\partial G/\partial n_i)_{T,P,n_j \neq n_i} = \bar{G}_i$. Expressions for γ_i must assure thermodynamic consistency as (Guggenheim, 1967)

$$\frac{\partial \ln \gamma_i}{\partial m_j} = \frac{\partial \ln \gamma_j}{\partial m_i}. \tag{S2}$$

The model parameters in the $G = f(m_i)$ function are obtained by fitting experimental values of the solution properties. In the case of electrolyte solutions, the measurements of the osmotic coefficient ϕ of water are typically used.

The osmotic coefficient ϕ is defined as the ratio between the observed osmotic pressure π_{obs} for the solution and the expected osmotic pressure π_{id} as if it was an ideal solution of same composition at the same temperature (no aggregation or dissociation processes considered). It allows to calculate the activity of water in the solution as

$$\phi \equiv \frac{\pi_{\text{obs}}}{\pi_{\text{id}}} = \frac{\ln a_1}{\ln x_1} = -\frac{s}{\sum_{i>1} m_i} \ln a_1. \tag{S3}$$

The osmotic coefficient can be also estimated in terms of other colligative properties, as the ratio of the water freezing point depression of the real solution θ_{obs} and its equivalent value in an ideal solution θ_{id}, and also as the ratio of the water relative vapor pressure depression $\Delta p_{\text{obs}}/p_1^o$ and $\Delta p_{\text{id}}/p_1^o$.

To assure thermodynamic consistency, the expressions from the activity coefficients derived from the model of $G = f(m_i)$ must satisfy the Gibbs–Duhem equation as

$$\begin{aligned} s d\mu_1 + \sum_{i>1} m_i d\mu_i &= RT s d\ln a_1 + RT \sum_{i>1} m_i d\ln a_i = 0 \\ &= RT d\left(m\phi\right) + RT \sum_{i>1} m_i d\ln a_i = 0. \end{aligned} \tag{S4}$$

The equation (S4) help us to correlate the nonidealities of the water behaviour in solution (experimentally determined in terms of the osmotic coefficient ϕ), with the nonidealities of the electrolytes γ_i as

$$d\left(m\phi\right) = -RT \sum_{i>1} m_i d\ln a_i = -RT \sum_{i>1} m_i d\ln\left(\gamma_i m_i\right), \tag{S5}$$

where $m = \sum_{i>1} m_i$ in molar or ionic concentration units. This equation can be also rearranged as

$$d\left((\phi - 1)\sum_{i>1} m_i\right) = -RT \sum_{i>1} m_i d\ln\left(\gamma_i\right). \tag{S6}$$

The equation (S6) is the key to find the parameters of the model $G = f(m_i)$. Once this equation is integrated to satisfy the conditions at the reference state, the integral solution is used in a regression analysis where the model parameters are obtained from the best fitting to the experimental osmotic coefficient data.

2 The Pitzer's model for multielectrolyte systems

Since the CISA (CMC-based ionic surfactant activity model) was built on the basis of the Pitzer's model for multielectrolyte systems, is necessary to highlight its key assumptions. The Pitzer's model, referred herein as the P-model, is based on the McMillan's idea of using virial coefficients to describe nonidealities coming from interactions in solutions between pairs of molecules, triplets of molecules, etc. (McMillan and Mayer, 1945). Instead of using the total Gibbs free energy, the departure from the ideal solution is calculated by means of the excess Gibbs free energy G^{Ex}. This variable shows the difference between the thermodynamic property of the solution and the value that could have if it was an ideal solution of equivalent concentration at the same temperature and pressure. The expression for G^{Ex} include the deviations caused by the long-range or Coulombic forces acting among ions in terms of the Debye–Hückel limiting law. It also uses a series of terms of increasing power of molality to represent the short-range pair and triple interactions. Each virial coefficient can be considered as an indicative of the interionic potentials of mean force in the solvent and it is found by fitting experimental data. The expression for the excess Gibbs free energy is given by Pitzer (2017) as

$$\begin{aligned}\frac{G^{Ex}}{n_1 RT} =& f^{\phi} + 2\sum_c\sum_a m_c m_a \left(B_{ca} + EC_{ca}\right) \\ &+ \sum_c\sum_{c'} m_c m_{c'} \left(\theta_{cc'} + \frac{1}{2}\sum_a m_a \psi_{cc'a}\right) \\ &+ \sum_a\sum_{a'} m_a m_{a'} \left(\theta_{aa'} + \frac{1}{2}\sum_c m_c \psi_{caa'}\right),\end{aligned} \tag{S7}$$

where m stands for molality and sub indices c and a indicate cations and anions, respectively. The variable E is the total equivalent electrical molality defined as $E = \sum_{i=\text{cations}} m_i|z_i|$ in terms of the cations or $E = \sum_{i=\text{anions}} m_i|z_i|$ in terms of the anions. The variable B_{ca} measures deviations coming from all possible binary interactions between ions c and a from the pure electrolyte ca. The variable $\theta_{cc'}$ represents the difference between total binary interactions and cation–cation cc' interactions, and the variable $\theta_{aa'}$ represents the difference between total binary interactions and anion–anion aa' interactions. C_{ca} considers all possible triplet interactions between ions c and a from the pure electrolyte ca, and in the same way than before, $\psi_{cc'a}$ and $\psi_{caa'}$ represent differences between interaction of unlike ions of the same sign from the average of interactions of like ions. The principal effects arise from pure electrolyte parameters B_{ca} and C_{ca} and interactions between three ions of the same sign are considered as unlikely and therefore disregarded (Pitzer and Kim, 1974).

The term $f^{\phi} = f^{\gamma}/3$ comes from the Debye–Hückel limiting law and depends on the solution ionic strength as

$$f^{\gamma} = -A_{\phi}\left(\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right), \tag{S8}$$

where b is a model parameter equal to 1.2 $\mathrm{kg}^{0.5}$ $\mathrm{mol}^{-0.5}$ equal for all electrolyte systems (Pitzer, 2017).

The ionic strength is defined as $I = 0.5\sum z_i^2 m_i$, where z_i is the ion valence. In the case of micelles their valence is usually corrected by a screening factor δ (Burchfield and Woolley, 1984).

The interaction parameters between an anion a and a cation c depend on the ionic strength of the solution as

$$B_{ca}^{\phi} = 2\beta_{ca}^{(0)} + \beta_{ca}^{(1)}\exp\left(\alpha_1\sqrt{I}\right), \tag{S9a}$$

$$B_{ca}^{\gamma} = 2\beta_{ca}^{(0)} + \frac{2\beta_{ca}^{(1)}}{\alpha_1^2 I}g\left(\alpha_1\sqrt{I}\right), \tag{S9b}$$

$$B_{ca}^{\prime\gamma} = \frac{2\beta_{ca}^{(1)}}{\alpha_1^2 I}\left(-1+\left(1+\alpha_1\sqrt{I}\right)\exp\left(-\alpha_1\sqrt{I}\right)\right), \tag{S9c}$$

and

$$C_{ca}^{\gamma} = \frac{3}{2}C_{ca}^{\phi} \tag{S9d}$$

where

$$g(x) = 1-\exp(-x)\left(1+x+\frac{x^2}{2}\right), \tag{S9e}$$

and α_1 is a model parameter equal to 2.0 $\mathrm{kg}^{0.5}$ $\mathrm{mol}^{-0.5}$ for all electrolyte systems. $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and C_{ca}^{ϕ} are model parameters that can be found by fitting experimental measurements of the osmotic coefficient or mean activity coefficients.

3 The Burchfield and Woolley activity coefficient model for aqueous surfactant-salt solutions, BW model

Activity coefficients for each one of the ionic species in solution $\mathrm{X}^-, \mathrm{M}^+, \mathrm{Mic}^{n-q}$ are calculated by combination of the simple Debye–Hückel term based the ion-size b parameters with molality weighted binary interaction parameters. Interaction parameters represent specific ion–ion interactions and account for deviations from the Debye–Hückel law. Interaction parameters are considered to be symmetric and negligible if correspond to ions of the same electric charge according to the principle of specific interactions of ion by Brønstead (Guggenheim, 1967). The model also uses the screening factor δ to consider the effect of the micellar charge on the ionic strength of the solution (Burchfield and Woolley, 1984).

The functional form of the excess Gibbs free energy of the aqueous solution with multiple ionic species (c for cations and a for anions) is (Pitzer, 1973)

$$\frac{G^{Ex}}{n_1 RT} = -\frac{4}{3} A^{\gamma} I^{\frac{3}{2}} \tau\left(\sqrt{I}\right) + 2\sum_{c}\sum_{a} B_{ca} m_c m_a, \tag{S10a}$$

with

$$\tau(x) = \left(\frac{3}{x^3}\right)\left(1 + x - \frac{1}{1+x} - 2\ln(1+x)\right). \tag{S10b}$$

Burchfield's model expressions of the activity coefficient of each cation (c) and anion (a) in solution are

$$\log \gamma_c = -\frac{A^{\gamma} I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \sum_{a} B_{ca} m_a, \tag{S11a}$$

and

$$\log \gamma_a = -\frac{A^{\gamma} I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \sum_{c} B_{ca} m_c, \tag{S11b}$$

where B_{ca} are composition–independent interaction parameters for each different cation–anion interaction among the ionic species in solution and A^{γ} is the Debye-Hückel limiting slope equal to 1.173740463035452 $\mathrm{kg}^{0.5}\ \mathrm{mol}^{-0.5}$ at 298.15 K.

4 Fittings for the osmotic coefficient of water in aqueous surfactant solutions

The experimental data used to calculate activity coefficients of aqueous solutions of ionic surfactants of atmospheric relevance is given in the next sections. In the case of aqueous surfactant solutions (no salt added), experimental values of ϕ^{mol} are fitted to rational or polynomial functions that describe the ratio of (ϕ^{mol}-1) / $\sqrt{m}$. These functions were used to find the mean ionic activity coefficient of the surfactant as

$$\ln \gamma_{2,\pm} = \phi^{\mathrm{mol}} - 1 + 2\int_0^{m_2} \frac{\phi^{\mathrm{mol}} - 1}{\sqrt{m}} d\sqrt{m}. \tag{S12}$$

The integral was solved numerically and the fitting obtained are in sections 4.1-4.3 of this document. Because it is very difficult to obtain reliable experimental data at infinite dilution when $m_2 \to 0$, it is better to impose the condition proved by the Debye–Hückel theory at this limiting state $\phi \to 1 - A^{\phi}$ as $m_2 \to 0$ (Pitzer, 2017).

4.1 Aqueous solutions of sodium octanoate (NaOct)

The integrand function fitted to the experimental data of NaOct at 298.15 K from Smith and Robinson (1942) is given as

$$\frac{\phi - 1}{\sqrt{m}} = \frac{-0.4013\sqrt{m}^3 + 0.2483m + 0.1072\sqrt{m} - 0.07257}{m^2 - 1.898\sqrt{m}^3 + 2.087m - 1.362\sqrt{m} + 0.4305} \tag{S13}$$

Table S1 Osmotic Coefficient of water and activity coefficient of sodium octanoate as a function of the surfactant molality at 298.15 K (Smith and Robinson, 1942)

m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$
0.1	0.9470	0.8429
0.2	0.9550	0.8201
0.3	0.9680	0.8182
0.5	0.8820	0.7294
0.6	0.8020	0.6547
0.7	0.7220	0.5824
0.8	0.6440	0.5161
0.9	0.5680	0.4571
1.0	0.5350	0.4224
1.1	0.5090	0.3932
1.2	0.4860	0.3676
1.4	0.4480	0.3256
1.6	0.4200	0.2934
1.8	0.3940	0.2667
2.0	0.3860	0.2484
2.5	0.3870	0.2170
3.0	0.3940	0.1954

* calculated using eq. (S12)

Table S2 Osmotic Coefficient of water and activity coefficient of sodium octanoate as a function of the surfactant molality at 293.15 K (Ekwall et al., 1967)

m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$	m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$
0.0730	0.9350	0.8389	1.0590	0.4760	0.3639
0.1232	0.9390	0.8144	1.0900	0.4730	0.3620
0.1706	0.9340	0.7924	1.1450	0.4680	0.3447
0.2460	0.9410	0.7799	1.2660	0.4430	0.3179
0.3050	0.9450	0.7740	1.2820	0.4290	0.3113
0.3360	0.9400	0.7661	1.3890	0.4280	0.2967
0.3847	0.9310	0.7528	1.6200	0.3740	0.2559
0.4429	0.9010	0.7216	1.6340	0.3790	0.2558
0.4943	0.8550	0.6799	1.7890	0.3580	0.2365
0.5640	0.8040	0.6316	1.9790	0.3480	0.2194
0.6060	0.7610	0.5955	2.2310	0.3390	0.1887
0.6500	0.7100	0.5558	2.4610	0.3390	0.2012
0.7180	0.6920	0.5297	2.5790	0.3300	0.1814
0.7210	0.6580	0.5113	2.5900	0.3390	0.1825
0.8100	0.6090	0.4669	2.6830	0.3470	0.1798
0.8210	0.6190	0.4691	2.8700	0.3450	0.1717
0.8350	0.5940	0.4544	2.9270	0.3510	0.1706
0.8400	0.5720	0.4434	3.3700	0.3760	0.1598
0.9140	0.5670	0.4255	3.4650	0.3740	0.1567
0.9840	0.5310	0.3966	3.6940	0.3800	0.1514
0.9850	0.5160	0.3905	3.8390	0.3830	0.1482
1.0480	0.4760	0.3620	3.9390	0.3850	0.1461
–	–	–	4.0970	0.3890	0.1432

* calculated using eq. (S12)

Table S3 Osmotic Coefficient of water and activity coefficient of sodium decanoate as a function of the surfactant molality at 298.15 K (De Lisi et al., 1981)

m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^{*}_{2,\pm}$	m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^{*}_{2,\pm}$
0.01	0.9635	0.8918	0.13	0.8086	0.6504
0.02	0.9581	0.8618	0.14	0.7846	0.6254
0.03	0.9526	0.8418	0.15	0.7485	0.5938
0.05	0.9472	0.8252	0.16	0.6965	0.5537
0.06	0.9360	0.7972	0.17	0.6554	0.5211
0.07	0.9303	0.7845	0.18	0.6227	0.4940
0.08	0.9242	0.7722	0.19	0.5957	0.4708
0.09	0.9170	0.7595	0.2011^{+}	0.5800	0.4490
0.10	0.9021	0.7413	0.3014^{+}	0.4180	0.3110
0.11	0.8740	0.7131	0.3975^{+}	0.3360	0.2430
0.12	0.8371	0.6787	0.5035^{+}	0.2930	0.1990

* calculated using eq. (S12), $^{+}$ from (Sharma et al., 2011)

Table S4 Osmotic Coefficient of water and activity coefficient of sodium decanoate as a function of the surfactant molality at 298.15 K (Sharma et al., 2011)

m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^{*}_{2,\pm}$
0.0099	0.9790	0.8990
0.0251	0.9520	0.8510
0.0509	0.9490	0.8050
0.0748	0.9510	0.7770
0.1529	0.7160	0.5780

The integrand function fitted to the experimental data of NaOct at 293.15 K from Ekwall et al. (1967) is given as

$$\frac{\phi-1}{\sqrt{m}} = \frac{-0.2926\sqrt{m}^3 + 0.0921m + 0.1772\sqrt{m} - 0.08244}{m^2 - 2.404\sqrt{m}^3 + 2.971m - 1.823\sqrt{m} + 0.4728}, \tag{S14}$$

with r^2 =0.9932, adj-r^2 =0.9920, and SSE=0.005108.

4.2 Aqueous solutions of sodium decanoate (NaDec)

The integrand function fitted to the experimental data of NaDec at 298.15 K from De Lisi et al. (1981) is given as

$$\frac{\phi-1}{\sqrt{m}} = \frac{-0.6309m + 0.3837\sqrt{m} - 0.06576}{m - 0.7788\sqrt{m} + 0.1691}, \tag{S15}$$

with r^2 =0.9967, adj-r^2 =0.9957, and SSE=0.003231.

Table S5 Activity coefficient of sodium dodecylsulfate as a function of the surfactant molality at 298.15 K (Sasaki et al., 1975)

m_2 (mol kg^{-1})	$\gamma^*_{2,\pm}$	m_2 (mol kg^{-1})	$\gamma^*_{2,\pm}$
9.9159×10^{-5}	0.9318	0.0068	0.6887
1.9637×10^{-4}	0.8847	0.0075	0.6888
2.9841×10^{-4}	0.8546	0.0080	0.6889
3.9452×10^{-4}	0.8254	0.0097	0.5580
4.8641×10^{-4}	0.8041	0.0148	0.3694
5.8325×10^{-4}	0.7833	0.0200	0.2789
6.8957×10^{-4}	0.7699	0.0302	0.1930
7.8204×10^{-4}	0.7500	0.0396	0.1470
8.6241×10^{-4}	0.7371	0.0505	0.1212
9.7760×10^{-4}	0.7321	0.0608	0.1017
0.0029	0.7002	0.0713	0.0891
0.0039	0.7005	0.0823	0.0781
0.0049	0.7007	–	–

4.3 Aqueous solutions of sodium dodecylsulfate (NaDS)

The integrand function fitted to the experimental data of NaDS at 298.15 K from Widera et al. (2003) is given as

$$\frac{\phi-1}{\sqrt{m}} = \frac{-0.1899m - 0.5606\sqrt{m} - 0.008277}{m - 0.1585\sqrt{m} + 0.02281}, \tag{S16}$$

with r^2 =0.9972, adj-r^2 =0.9970, and SSE=0.129.

4.4 Aqueous solutions of sodium decanoate and sodium chloride

Table S7 compiles the mean ionic activity coefficients reported by Sharma et al. (2011) for sodium decanoate and sodium chloride in aqueous solutions at 298.15 K. These values were used as shown here to fit the parameters of the CISA model.

5 Calculation approaches for the fraction of micellization

The equilibrium constant for the micellization reaction is given as

$$K = \frac{a_{\mathrm{Mic}}}{a_{\mathrm{M}}^q a_{\mathrm{X}}^n} = \frac{\gamma_{\mathrm{Mic}}}{\gamma_{\mathrm{M}}^q \gamma_{\mathrm{X}}^n} \frac{m_{\mathrm{Mic}}/m^o_{\mathrm{Mic}}}{\left(m_{\mathrm{M}}/m^o_{\mathrm{M}}\right)^q \left(m_{\mathrm{X}}/m^o_{\mathrm{X}}\right)^n}, \tag{S17}$$

where m_i^o represents the molality of ionic species i at the reference state of 1 mol kg^{-1} where $\gamma_i = 1$. This equation must be solved with the help of an activity coefficient model to find the fraction of surfactant ions that transform into micelles $\xi = nm_{Mic}m_2$ or fraction of micellization. Values for the equilibrium constant of micellization are reported in Table S8.

Table S6 Osmotic Coefficient of water and activity coefficient of sodium dodecylsulfate as a function of the surfactant molality at 298.15 K (Widera et al., 2003)

m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$	m_2 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$
0.010	0.6220	0.4476	0.7530	0.1350	0.0093
0.020	0.3360	0.2386	0.8730	0.1240	0.0081
0.030	0.2460	0.1658	0.8750	0.1280	0.0081
0.040	0.2030	0.1273	0.8980	0.1180	0.0078
0.050	0.1760	0.1031	0.8990	0.1200	0.0078
0.100	0.1320	0.0540	0.9780	0.1240	0.0073
0.150	0.1200	0.0372	0.9960	0.1350	0.0073
0.200	0.1180	0.0288	0.9980	0.1260	0.0072
0.250	0.1140	0.0236	1.0000	0.1250	0.0072
0.257	0.1200	0.0232	1.0430	0.1160	0.0068
0.273	0.0910	0.0214	1.0490	0.1370	0.0070
0.273	0.1740	0.0232	1.0510	0.1150	0.0068
0.294	0.1300	0.0208	1.0640	0.1240	0.0068
0.297	0.1550	0.0212	1.0650	0.1210	0.0068
0.300	0.1160	0.0202	1.0720	0.1190	0.0067
0.350	0.1140	0.0176	1.2000	0.1260	0.0061
0.400	0.1160	0.0157	1.2240	0.1100	0.0059
0.450	0.1190	0.0142	1.2270	0.1320	0.0060
0.500	0.1180	0.0130	1.2780	0.1250	0.0058
0.506	0.1250	0.0129	1.2820	0.1280	0.0058
0.507	0.0990	0.0126	1.4000	0.1230	0.0053
0.513	0.1010	0.0125	1.4160	0.1130	0.0052
0.515	0.1260	0.0128	1.4190	0.1190	0.0052
0.540	0.1360	0.0124	1.4480	0.1080	0.0051
0.542	0.1260	0.0128	1.4530	0.1250	0.0052
0.555	0.1200	0.0119	1.5580	0.1400	0.0049
0.557	0.1600	0.0123	1.6020	0.1190	0.0047
0.704	0.1290	0.0098	1.6080	0.1220	0.0047
0.742	0.1310	0.0093	1.7550	0.1050	0.0043
0.750	0.1230	0.0092	1.7590	0.1140	0.0043
0.752	0.1280	0.0092	1.7840	0.1160	0.0042
–	–	–	1.7900	0.1160	0.0042

* calculated using eq. (S12)

Instead of solving K to find ξ, we can use the approach of the pseudo–phase separation method to estimate its value using the concentration-dependent parameterization of the CMC as a function of the salt molality (De Lisi et al., 1981)

$$\xi = \left(\frac{(\text{sgn}\,(\text{CMC} - m_{\text{MX}}) + 1)}{2} \right) \frac{m_{\text{MX}} - \text{CMC}}{m_{\text{MX}}}, \tag{S18}$$

where CMC is the surfactant critical micelle concentration in molal units and sgn is the sign function.

We did not found significant differences between these approaches after comparing the fraction of the surfactant moles micellized as a function of the surfactant molality in solution as shown in Fig. S1 for aqueous solutions of NaDec and in Fig. S2 for aqueous solutions of NaDec and NaCl. However this finding is highly dependent on the CMC value used to calculate ξ. Fig. S1 shows the results using the CMC value reported by two different studies at the same temperature.

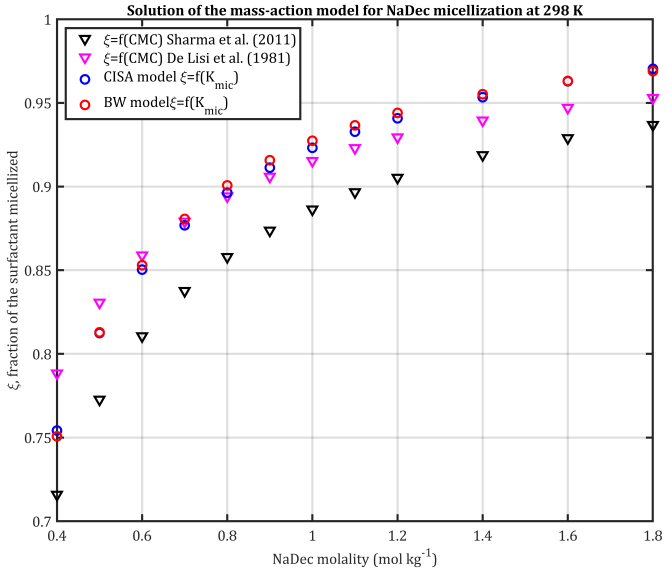

Fig. S1 Fraction of micellization *xi* of NaDec in aqueous solutions at 298.15 K calculated with the CMC–approach and solving the mass–action model with the activity coefficients from the CISA model and the BW model

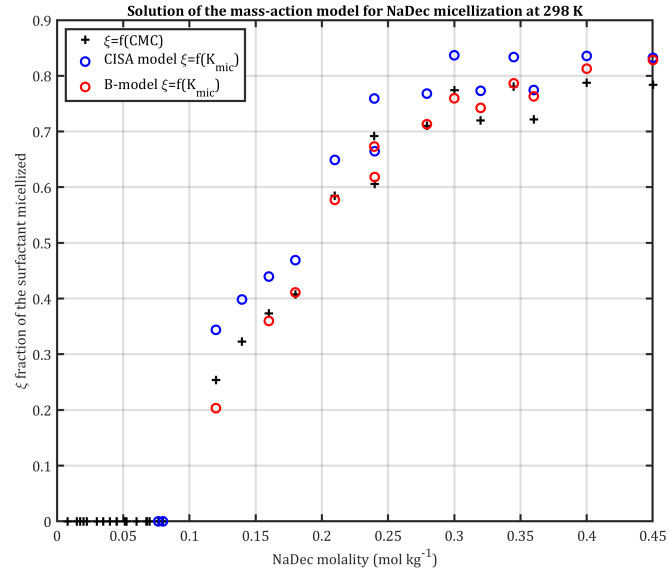

Fig. S2 Fraction of micellization *xi* of NaDec in aqueous solutions containing NaDec and NaCl at 298.15 K calculated with the CMC–approach and solving the mass–action model with the activity coefficients from the CISA model and the BW model

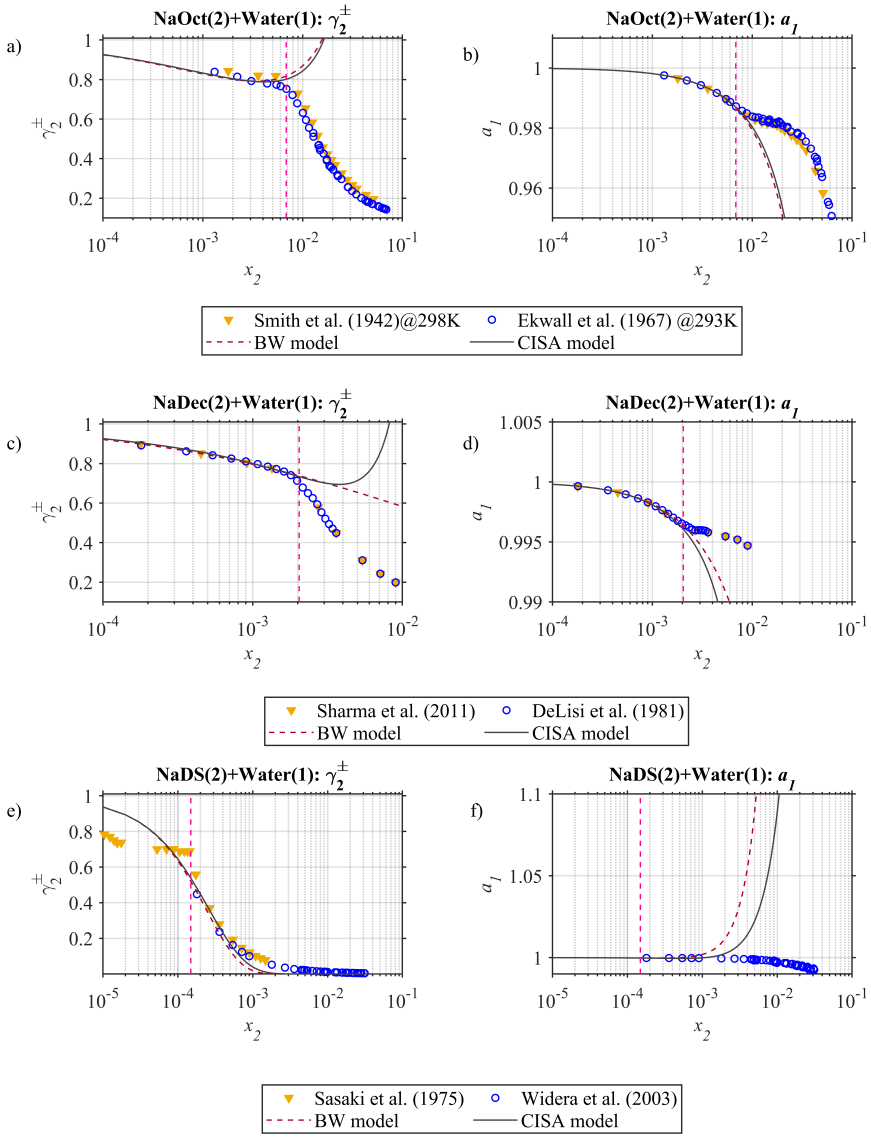

Fig. S3 Mean ionic activity coefficients of ionic surfactants and water activity in aqueous solutions (a,b) NaOct (c,d) NaDec (e,f) NaDS. Experimental values and calculated values from the CISA model and the BW model disregarding micellization. The CMC is in each case depicted by a pink vertical line. Experimental data for validation purposes is shown with yellow triangles. Experimental data for fitting model parameters is shown with blue circles

Table S7 Osmotic Coefficient of water and activity coefficient of sodium decanoate and sodium chloride as a function of the surfactant molality and salt molality at 298.15 K (Sharma et al., 2011)

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	ϕ^{mol}	$\gamma^*_{2,\pm}$	$\gamma_{3,\pm}$
0.0225	0.0025	0.9270	0.8520	0.8520
0.0450	0.0050	0.8960	0.8520	0.8520
0.0675	0.0075	0.8890	0.7770	0.7770
0.0765	0.0085	0.8850	0.7670	0.7670
0.1800	0.0200	0.6150	0.4810	0.6300
0.3600	0.0400	0.3670	0.2600	0.5380
0.4500	0.0500	0.3440	0.2160	0.5250
0.0081	0.0020	0.9620	0.8980	0.8980
0.0200	0.0050	0.9320	0.8520	0.8520
0.0400	0.0100	0.9160	0.8070	0.8070
0.0600	0.0150	0.9070	0.7770	0.7770
0.0800	0.0200	0.8930	0.7540	0.7540
0.1600	0.0400	0.6780	0.5140	0.6460
0.2399	0.0600	0.5430	0.3600	0.5850
0.3199	0.0800	0.4770	0.2810	0.5580
0.4000	0.1000	0.4410	0.2340	0.5450
0.0175	0.0075	0.9220	0.9770	0.9770
0.0350	0.0150	0.9090	0.8070	0.8070
0.0525	0.0225	0.9180	0.7770	0.7770
0.0699	0.0301	0.9010	0.7540	0.7540
0.1397	0.0601	0.7500	0.5540	0.6620
0.2098	0.0901	0.5960	0.3890	0.6020
0.2793	0.1200	0.5470	0.3060	0.5750
0.3449	0.1483	0.5200	0.2580	0.5620
0.0150	0.0100	0.9780	0.9550	0.9550
0.0300	0.0200	0.9570	0.8070	0.8070
0.0451	0.0301	0.9390	0.7760	0.7760
0.0511	0.0341	0.9390	0.7670	0.7670
0.0600	0.0400	0.9430	0.7540	0.7540
0.1200	0.0799	0.8280	0.6000	0.6760
0.2396	0.1594	0.6480	0.3350	0.5900
0.3000	0.2000	0.6070	0.2800	0.5750

Table S8 Equilibrium constants for the micellization reaction in aqueous solutions of ionic surfactants

System	Temperature (K)	K	Range mol kg^{-1}
Water–NaOct[a]	293.15 (298.15)	22.0 (26.0)	0.07–4.1 (0.01–3.2)
Water–NaDec[a]	298.15	140	0.01–0.19
Water–NaDS[a]	298.15	548	0.006–0.27
Water–NaDec–NaCl[b]	298.15	144	0.0081–0.5035

[a] (Burchfield and Woolley, 1984), [b] (Sharma et al., 2011)

6 Temperature–dependent parametrizations for CISA's model parameters

We built temperature-dependent function for the parameters β^0_{NaCl}, β^1_{NaCl} and C^{ϕ}_{NaCl} using the values reported by Pitzer et al. (1984) to describe the nonidealities of aqueous solutions of NaCl at 1 bar between 273 K and 313 K. The expressions to calculate

these model parameters are

$$\beta^0_{\mathrm{NaCl}} = 0.0839\exp(0.0005417T) - 205.8\exp(-0.03062T), \tag{S19a}$$

$$\beta^1_{\mathrm{NaCl}} = 0.1067\exp(0.003075T), \tag{S19b}$$

$$C^{\phi}_{\mathrm{NaCl}} = 2\left(-5.894\times10^{-5}\exp(0.009207T) + 13.38\exp(-0.03037T)\right), \tag{S19c}$$

where T is in kelvin.

While there is a wide spectrum of data about osmotic coefficients in aqueous solutions of inorganic electrolytes at different temperatures, this type of data for aqueous surfactant solutions of atmospheric relevance is scarce. We found a single set of temperature–dependent data of osmotic coefficients in aqueous solutions of NaDec presented by De Lisi et al. (1981). The CISA model parameters were fitted at three temperature levels, 278.15 K, 288.15K and 298.15 K. Results of the fittings are shown in Fig. S4.

Fig. S5 shows the temperature–dependence of the CISA model parameters β^0_{NaDec}, β^1_{NaDec} and $C^{\phi}_{\mathrm{NaDec}}$, β^0_{NaMic}, β^1_{NaMic} and $C^{\phi}_{\mathrm{NaMic}}$ in the range between 288 K and 298 K. We observed U-shape curves for the model parameters related to ion–micelle interactions. This U-shape behaviour has been observed in temperature–dependent parametrizations of the critical micelle concentration for ionic surfactants and related to the existence of a turning point in the enthalpy of micellization that switches from exothermic to endothermic conditions at a characteristic temperature $T*$. The minimum in the U-shape curve occurs at $T*$ and corresponds to the temperature at which the free energy of micelle formation is due only to entropic contributions (La Mesa, 1990; Onori et al., 1994).

We used linear extrapolation to calculate the CISA model parameters and used them to predict the mean ionic activity coefficient of NaDec and the osmotic coefficient in aqueous solutions at 273.15 K. Results from the CISA model were compared to experimental data presented by Sharma et al. (2011) in Fig. S6. We notice a very good agreement between calculated and experimental values up to 0.25 mol kg^{-1} above the CMC, but there are important deviations at higher surfactant molalities in the solution. To explain these differences we must consider two important factors. First, the experimental data of osmotic coefficients was measured at the solution freezing temperatures and then converted to values at 273 K, therefore it is likely that this introduced a source of variance. Second, the Krafft point for NaDec in aqueous solutions is 275.24 K (Blanco et al., 2005), above 273 K, therefore our calculations represent a hypothetical state below the water solubility limit of the surfactant.

We used the CISA model to represent the activity coefficients and the water activity in aqueous solutions of NaDec and NaCl at 273.15 K using the model parameters defined for water–NaCl and water–NaDec systems and a composition-dependent function for the CMC at this temperature. The CMC parametrization was based on the experimental values reported by Sharma et al. (2011) and depends on the NaCl molality as

$$\mathrm{CMC} = \frac{0.06746}{0.4589 + m_3}, \tag{S20}$$

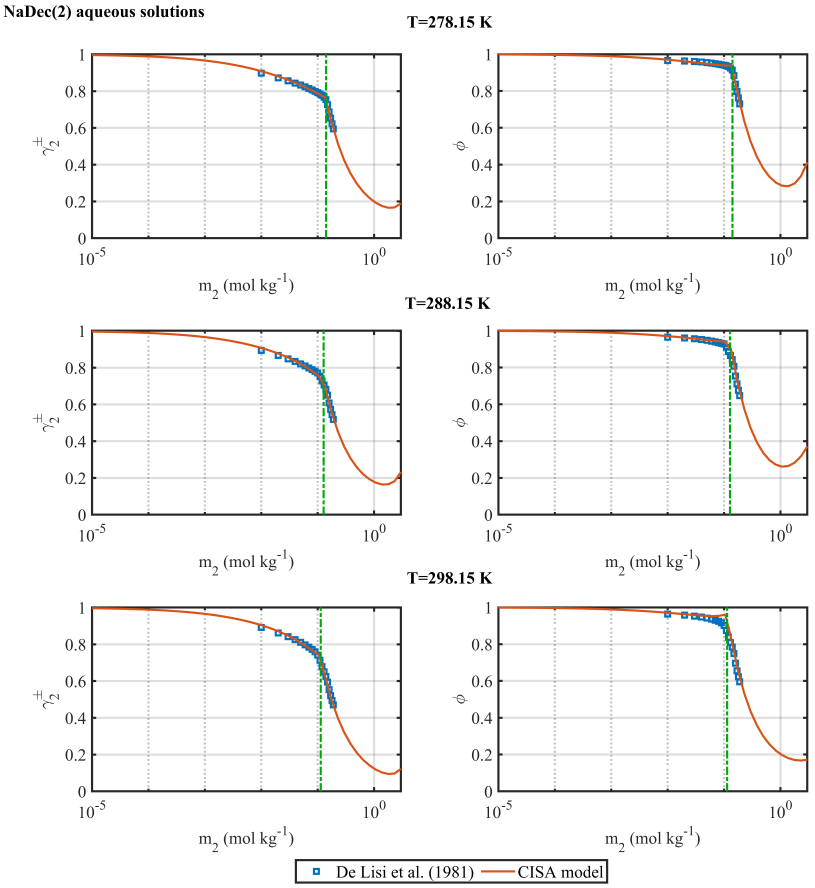

Fig. S4 Surfactant mean ionic activity coefficient and osmotic coefficient in NaDec aqueous solutions at different temperatures calculated with the CISA model. Model parameters were fitted to the experimental data of De Lisi et al. (1981)

where m_3 is the molality of NaCl. Indicators for the quality of the fitting are $r^2 = 0.8694$, $r^2_{adj} = 0.8259$ and the relative mean squared error $RMSE = 0.003887$.

Fig. S7 how the CISA model follows the trends of the experimental surfactant activity coefficients at all the surfactant–salt mixing ratios, but tends to overpredict the values of the salt mean ionic activity coefficient at concentrations above the CMC. This overprediction has an small effect on the water activity values as it is shown in Fig. S8. These deviations from experimental data could indicate the existence of stronger ion–micelle interactions in ternary water–surfactant–salt solutions than those observed in binary solutions related to the counterion binding process. Also it could indicate a subestimation of the Na–Mic model parameters in the binary water–NaDec solutions. We already mentioned the existence of increasing deviations of the CISA's calculations with increasing surfactant molalities in binary water–NaDec solutions.

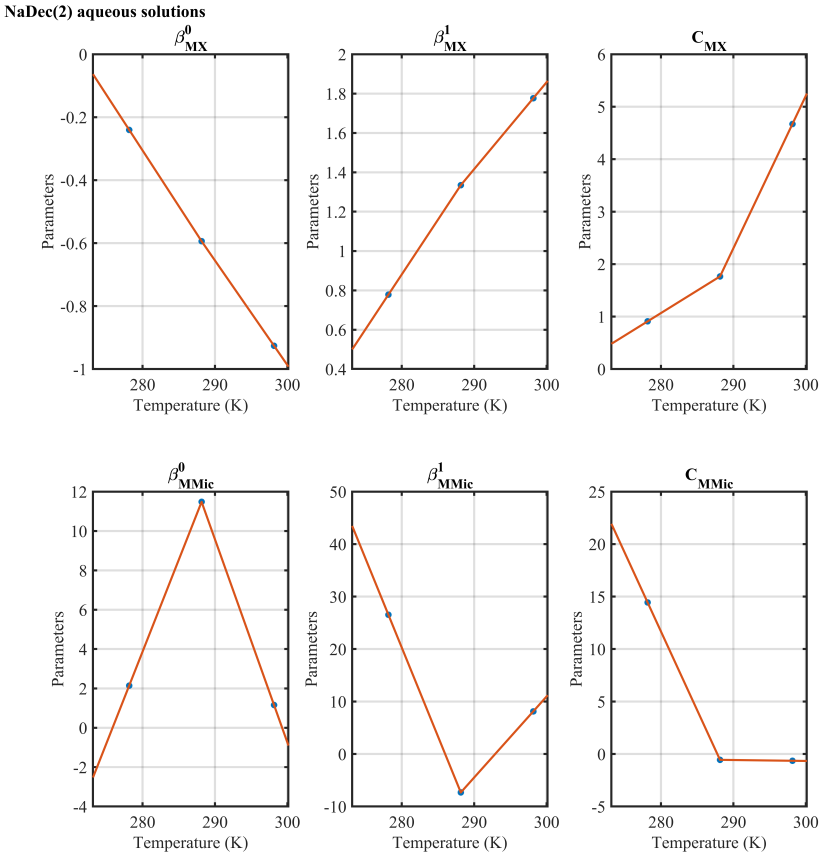

Fig. S5 Temperature–dependence of the CISA's model parameters in NaDec aqueous solutions

We noticed that the experimental data of osmotic coefficients was measured at the solution freezing temperatures and then converted to values at 273 K, therefore it is likely that this introduced a source of variance.

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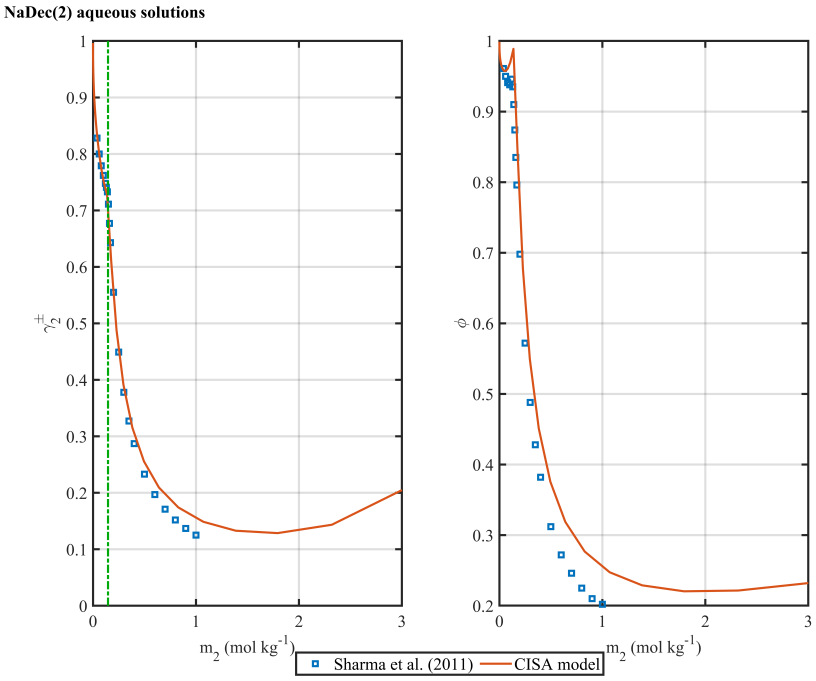

Fig. S6 Surfactant mean ionic activity coefficient and osmotic coefficient in NaDec aqueous solutions at 273.15 K calculated with the CISA model against experimental data of Sharma et al. (2011)

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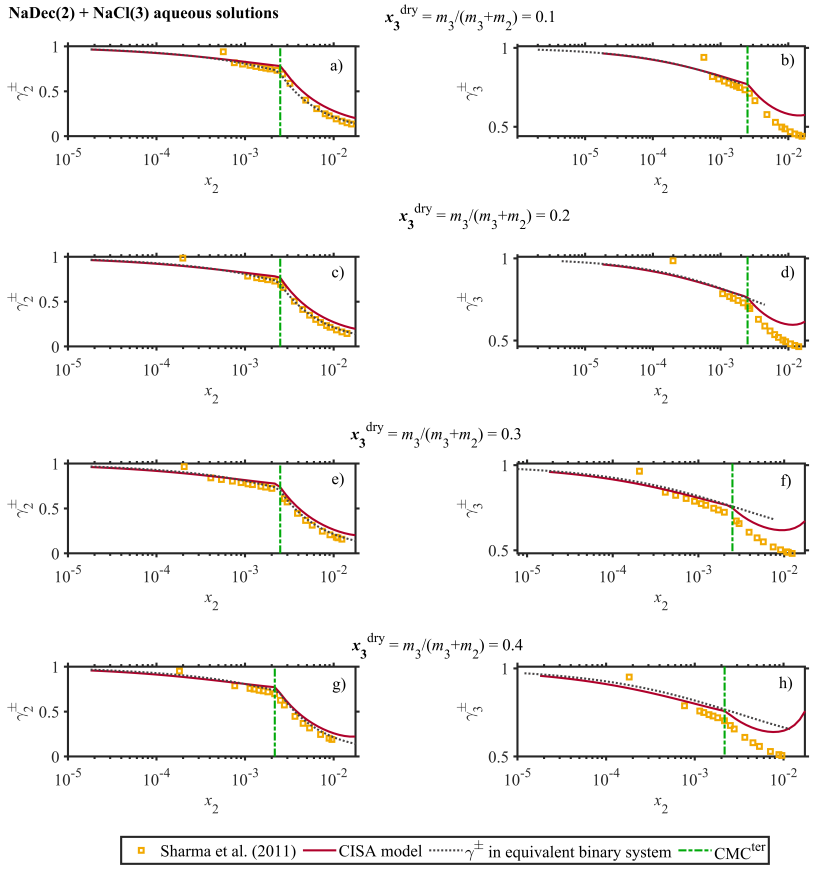

Fig. S7 Calculated values of the mean ionic activity coefficients of NaDec and NaCl in aqueous solutions at different mixing ratios compared to experimental values from Sharma et al. (2011) at 273 K. The CMC^{ter} indicates the critical micelle concentration in the ternary water–surfactant–salt system (Eq. S20).

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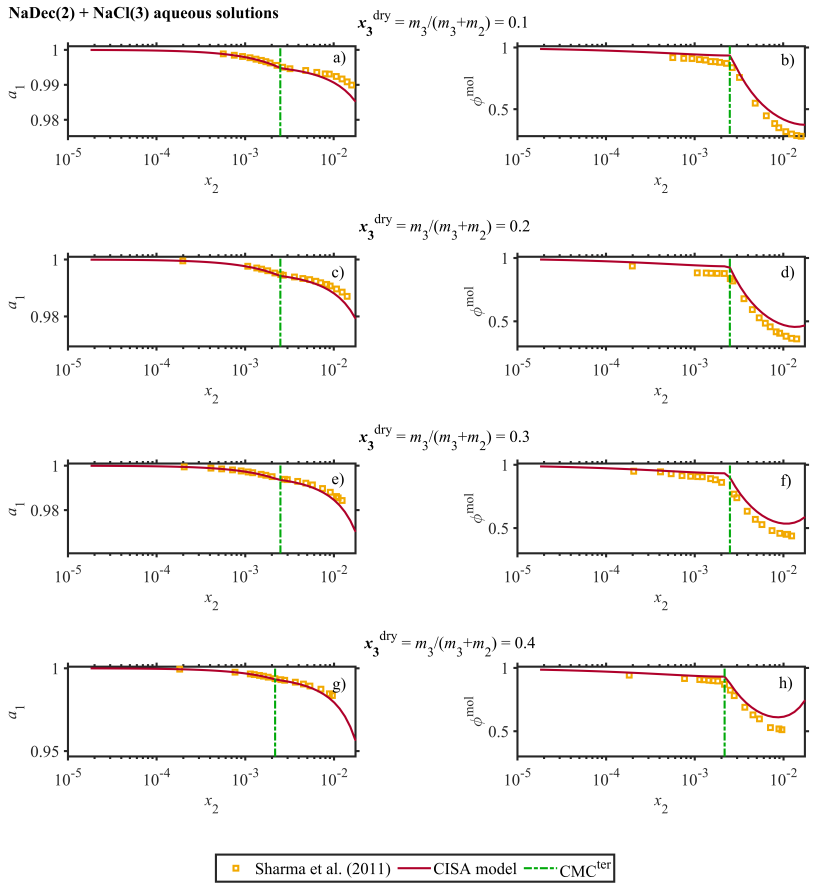

Fig. S8 Calculated values of the activity and osmotic coefficient of water in NaDec–NaCl aqueous solutions at different mixing ratios compared to experimental values from Sharma et al. (2011) at 273 K. The CMC^{ter} indicates the critical micelle concentration in the ternary water–surfactant–salt system (Eq. S20).

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