

1. Definition of the characteristic distance d_{EV} .

A surface excess Γ of surfactant at the air-water interface can be converted into a concentration within the layer of liquid of thickness δ equal to the length of a surfactant monomer. For SDS δ would be about 3 nm. A distance d_{EV} can be calculated for SDS ions at the interface as:

$$d_{EV} = 0.5S^{1/2} = 0.5[10^{24}(\text{nm}/l)/(\delta \sum [C_S]N_A)]^{1/2} \quad (1)$$

Here $[C_S]$ is the concentration of surfactant which is numerically equal to Γ , and S the surface per surfactant ion (not the surfactant's head surface), calculated from the volume element V_S occupied by a surfactant monomer at the interface from

$$V_S = 10^{24}(nm/l)/(\sum [C_S]N_A) = \delta S_S \quad (2)$$

d_{EV} is the semi-distance between same-charge ions, and therefore an estimate of the average distance to a counter ion which would necessarily be in between them due to a balance of repulsive and attractive forces in the solution⁵. This distance can be compared with Bjerrum's critical distance for ionic pair association given as

$$d_{Bj} = \frac{z_+ |z_-| e^2}{8\pi \epsilon_0 \epsilon_r kT} \quad (3)$$

Here k is Boltzmann's constant, T the temperature in K, ϵ_0 and ϵ are the dielectric constants in the vacuum and in the solvent involved, e the charge of an electron and z the charges of the ions. If d_{EV} is smaller than d_{Bj} then ionic pairs will be likely to happen because counter ions will be within Bjerrum's distance for ionic pair association. The form of the equation to give the characteristic distance to a counter ion in the bulk phase is given as equation 4.

$$d_{EV} = 0.5 [10^{24} (\text{nm/l}) / (\sum [C_S] N_A)]^{1/3} \quad (4)$$

2. Calculation of the relative binding strength parameter γ .

Assuming that the mechanisms of micellization and binding are related, we deduce a parameter for the relative affinity of an alkali cation for a SDS micelle from the relative surface excesses Γ_{M^+} .

We define a relative strength parameter γ_{M^+} . We will take as reference $\gamma_{Na^+}=1$, and the rest of the coefficients as $\gamma_{M^+}=(\Gamma_{M^+}/\Gamma_{Na^+})^{3/2}$. From data by Lu et al¹², $\gamma_{Li^+}= 0.942$, $\gamma_{K^+}= 1.27$, $\gamma_{Rb^+}= 1.59$ and $\gamma_{Cs^+}= 1.45$ are trivially calculated. Because of the similarity of experimental behavior between H^+ and Na^+ , we assign $\gamma_{H^+}= 1$. The argument for the choice of the power 3/2 is that the relative interaction strength of the cations manifests itself in two dimensions over the air-water surface, but that in the solution the interaction strength takes place in three dimensions. The parameter is inspired in a control parameter proposed in a previous model⁵.

3. Prediction of Binding of Al^{3+} onto SDS micelles in the presence of 0.250M NaCl: comparison with binding of Al^{3+} in the absence of added electrolyte.

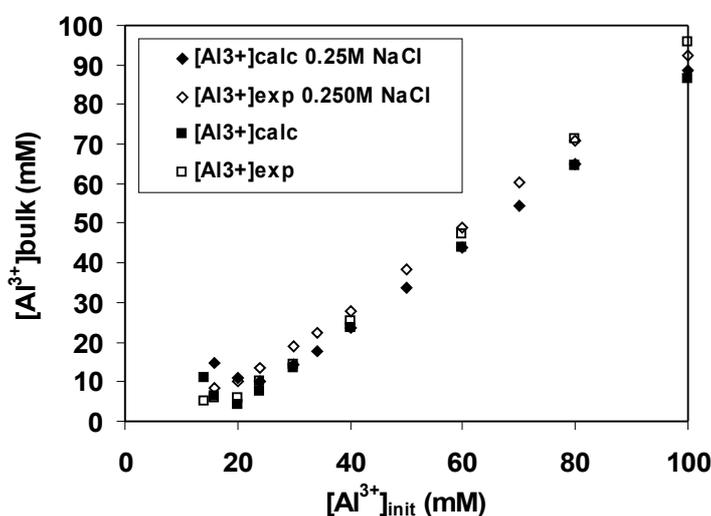


Figure 8. Prediction of free Al^{3+} in systems $\text{SDS}/\text{Al}_2(\text{SO}_4)_3$ and $\text{SDS}/\text{Al}_2(\text{SO}_4)_3/\text{NaCl}$

Figure 8 shows plots for free Al^{3+} concentration calculated from experiments on flocculation^{7,8} of SDS with $\text{Al}_2(\text{SO}_4)_3$ in the presence of NaCl. In this case the calculation is modified because the bound Al^{3+} concentration and the concentration in the SCR would account for all the Al^{3+} in the floc and in non-flocculated micelles. The results show that there is some under prediction of the bulk concentration of Al^{3+} in the presence of NaCl 0.250M. The model consistently predicts free Al^{3+} concentrations lower than the experimental for 0.250M NaCl. On the other hand, in the absence of NaCl, except above 60 mM of total Al^{3+} as discussed in previous work, the predictions fit very well with the experimental data. It has been suggested⁵ that the discrepancy above 60 mM Al^{3+} may be due to the transition from spherical (3-surfactant head clusters) to cylindrical (4-surfactant head clusters). This would reduce the availability of adsorption sites for Al^{3+} and result in a higher bulk phase concentration. The added NaCl may both increase somehow the competition of Na^+ ,

sequestering some Al^{3+} in complexes with chloride, and contributing to the overall salinity required to cause the transition between micellar shapes.

4. Prediction of competitive binding of Al^{3+} and Zn^{2+} onto SDS micelles.

We will study the case of the system $\text{SDS}/\text{ZnSO}_4/\text{Al}_2(\text{SO}_4)_3$ system, investigated mainly in connection with heavy metal disruption of micellar flocculation^{7,8,21} in a micelle-mediated separation technique named Adsorptive Micellar Flocculation²². In the experiments, Zn^{2+} was added first, and always in concentrations higher to the condition of saturation of the capacity of the micelles to adsorb Zn^{2+} . Al^{3+} was added subsequently, with concentrations indicated in Figures 9 and 10. Figure 9 shows data for $[\text{ZnSO}_4] = 0.031\text{M}$, and Figure 10 shows data for $[\text{ZnSO}_4] = 0.075\text{M}$.

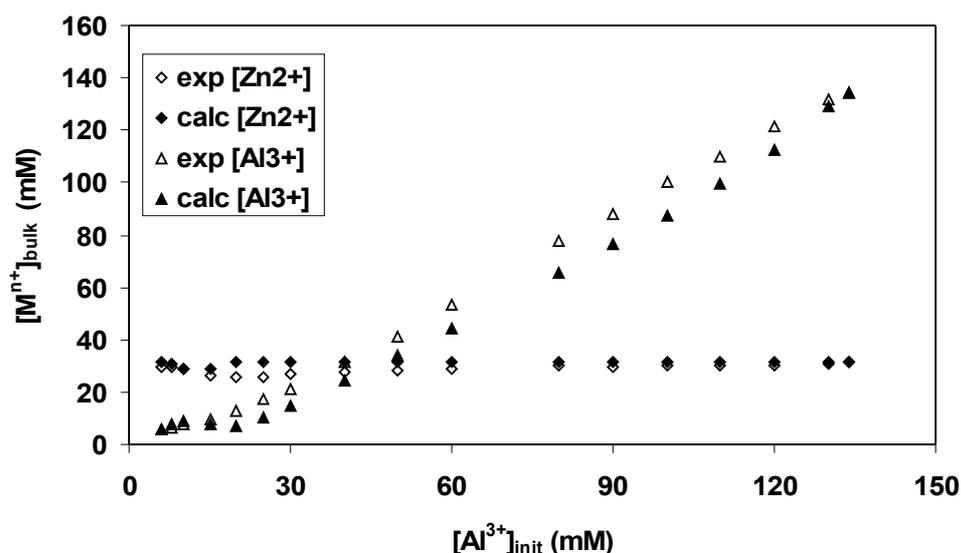


Figure 9. Experimental values of bulk concentration and model predictions for SDS 0.05M, ZnSO_4 0.031M and variable $\text{Al}_2(\text{SO}_4)_3$ concentrations

In Figure 9 the model underpredicts binding of Zn^{2+} as shown by the higher than experimental Zn^{2+} concentrations in the bulk phase at the lower concentrations of Al^{3+} . When the concentration of Al^{3+} raises the model predicts correctly the concentration of Zn^{2+} : zinc is fully displaced from the micelles and its concentration becomes constant. This is so because for the case $\text{M}^{2+}/\text{M}^{3+}$ we impose in the model that the lower charge cation behaves as

indifferently adsorbing and is displaced as if it was monovalent. It is important to take into account that in the experiments on micellar flocculation^{7,8,21} Zn^{2+} was added first to the micellar solution and then Al^{3+} . The coherence of the model predictions and the experimental results mean that it is correct to assume that Al^{3+} actually displaces Zn^{2+} from the ionic pairs. The over prediction in the binding of Al^{3+} (lower than experimental free Al^{3+} concentrations) has been previously connected with the hypothesis of spherical SDS micelles having a 3-surfactant basic cluster whereas cylindrical micelles would have a 4-surfactant basis cluster. As the concentration of electrolyte raises, a transition from spherical to cylindrical may in practice reduce the available binding “space”. The convergence at the highest Al^{3+} concentrations is simply due to the fact that there is no flocculation and the bulk phase concentrations become the nominal concentrations for all the species involved.

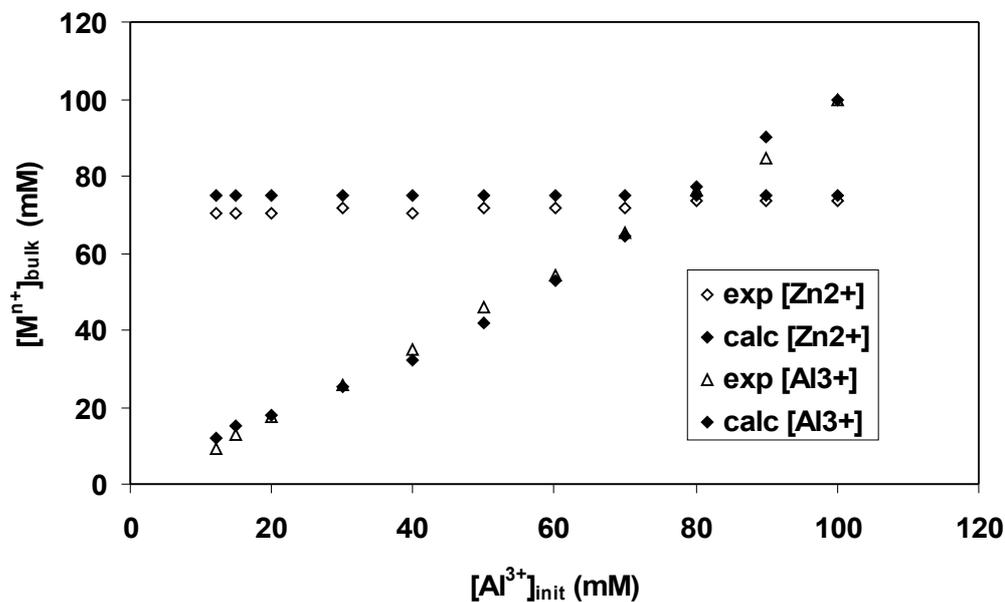


Figure 10. Predicted and experimental bulk phase concentrations of Al^{3+} and Zn^{2+} . SDS 0.05M, $ZnSO_4 = 0.075M$

Paradoxically, Figure 10 shows an anomaly in that the predictions are almost perfect. Considering the previous discussion, this should not be the case: the binding of Al^{3+} is higher than expected. What we know is that for the conditions corresponding to this figure, over all

the range of Al^{3+} concentrations both cations are well above their critical Bjerrum conditions for ionic pairing with SO_4^{2-} , their counterion in the electrolytes. A strong presence of ionic pairs $\text{Al}^{3+}:\text{SO}_4^{2-}$ and $\text{Zn}^{2+}:\text{SO}_4^{2-}$ would explain the apparent charge inversion reported on this system²¹, as those species would accumulate in the BR with higher concentration to cause the total charge neutralization. This would explain why the model seems to predict correctly: sulfate-paired Al^{3+} is not displaced from the BR as a polyvalent cation would, and a balance accounting only for the cations within the BR and forming ionic pairs and the micellar surfactant would yield higher.

Additional References.

(21) Paton, P.; Talens-Alesson, F. *Langmuir* **2002**, *18* (22), 8295–8301

(22) Porrás-Rodríguez, M. ; Talens-Ale3sson, F.I. *Environ. Sci. Technol.* **1999**, *33*(18), 3206-3209