

# Electronic Supplementary Information for: Stability of reverse micelles in rare-earth separation: a chemical model based on a molecular approach

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## S1 Justification of the calculation of the association constant

### S1.1 General ideas for the calculation of the association constant

We want to calculate from molecular dynamics the association constant of two solutes  $A$  and  $B$ . This quantity corresponds to the Mass Action Law (MAL) constant of the equilibrium



When a compound  $\alpha = A, B$  or  $C$  is diluted in the pure solvent, the chemical potential reads

$$\mu_\alpha = \mu_\alpha^\circ + k_B T \ln \frac{\rho_\alpha}{\rho^\circ}, \quad (2)$$

where  $\mu_\alpha^\circ$  is the standard chemical potential.  $\rho_\alpha$  is the concentration of species  $\alpha$ .  $k_B T = 1/\beta$  is Boltzmann's constant multiplied by the temperature and  $\rho^\circ$  is the concentration which defines the standard state (generally taken to correspond to  $1 \text{ mol L}^{-1}$ ). The association constant  $K^\circ$  is

$$K^\circ = \exp\left(\frac{-\mu_C^\circ + \mu_A^\circ + \mu_B^\circ}{k_B T}\right). \quad (3)$$

Consequently the problem consists in calculating this difference in terms of standard chemical potentials from first principles. For the sake of simplicity, we will first deal with simple atomic solutes and then with molecular solutes (interacting via *weak* interactions).

### S1.2 Atomic solute

Let us consider a dilute solute in a pure solvent described by the canonical ensemble. The partition function is

$$Z = \frac{1}{N_S! \Lambda_S^{3N_S} N! \Lambda^{3N}} \int d\mathbf{r}^N d\mathbf{r}_S^N \exp(-\beta V), \quad (4)$$

where  $N$  and  $\Lambda$  are the number and the de Broglie length of particles. If there is no index, the value corresponds to the solvent. The index  $S$  corresponds to the dilute solute particles.  $\mathbf{r}_S$  and  $\mathbf{r}$  correspond respectively to the positions of the solute and of the solvent in phase space. If the solvent is molecular,  $\mathbf{r}$  is replaced by the degrees of freedom of the solvent molecules and the solvent de Broglie length  $\Lambda$  is replaced by the corresponding integral

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over the conjugated variables. If  $Z_P$  is the partition function of the pure solvent, we obtain

$$\frac{Z}{Z_P} = \frac{1}{N_S! \Lambda_S^{3N_S}} \frac{\int d\mathbf{r}^N d\mathbf{r}_S^N \exp(-\beta V)}{\int d\mathbf{r}^N \exp(-\beta V)}. \quad (5)$$

At the thermodynamic limit, we can neglect edge effects. Moreover, if the solute is diluted, the solute/solute correlations can be neglected so that

$$\frac{Z}{Z_P} \approx \frac{V_S^N}{N_S! \Lambda_S^{3N_S}} \left( \frac{\int d\mathbf{r}^N \exp(-\beta V^1)}{\int d\mathbf{r}^N \exp(-\beta V)} \right)^{N_S}, \quad (6)$$

where  $V^1$  is the potential energy of a system with one immobile cation located at  $\mathbf{r}_S = \mathbf{0}$ . Then one can calculate the corresponding free energy and the various thermodynamical properties. The pressure is

$$P = P^p + \frac{N_S}{V} k_B T, \quad (7)$$

where  $P^p$  is the pressure of the pure solvent in the same volume which is at the thermodynamic limit the pressure of the solvent with the same chemical potential as in the solution. The second term corresponds to the osmotic pressure. The resulting chemical potential is given by Eq. 2 together with

$$\mu_S^\circ = 3k_B T \ln \Lambda_S - k_B T \ln a + k_B T \ln \rho^\circ, \quad (8)$$

we have

$$a = \frac{\int d\mathbf{r}^N \exp(-\beta V^1)}{\int d\mathbf{r}^N \exp(-\beta V)}. \quad (9)$$

This formula provides a method to calculate the standard chemical potential of an atomic solute because we only need to calculate the excess free energy when the solute is added to the solution. It is actually consistent with the method used to calculate excess Gibbs energy of ions in solutions (see e.g., Ref. <sup>1</sup>) where the ion potential is progressively added to the pure water from a thermodynamic integration. We need to generalize this strategy to molecular solutes.

### S1.3 Molecular solutes

Now the solute is characterized by the position of one of the atoms  $\mathbf{r}_S$  but further internal degrees of freedom exist. For example, one can consider the position of the other atoms with respect to  $\mathbf{r}_S$ . They are denoted by the variables  $\mathbf{r}'_S$ .

The previous calculations are globally valid but one has to add an integral over the internal variables  $\mathbf{r}'_S$ . The most important difference comes from the indistinguishable terms  $N!$  because now we have two kinds of indiscernibility: (i) inside the solutes and (ii) between the solutes. Let us consider that the solute is made of  $v_1$  particles 1,  $v_2$  particles 2

and so on. Generally, when every atom is considered explicitly the indiscernibility factor is

$$\frac{1}{\prod_i N_i!}, \quad (10)$$

with  $N_i = v_i N_S$ . Nevertheless we want to write a law in terms of the global solute. Then the indiscernibility should actually be

$$\frac{1}{N_S!} \frac{1}{(\prod_i v_i!)^{N_S}}. \quad (11)$$

The first term ( $1/N_S!$ ) corresponds to the indiscernibility between the molecular solutes and the second term  $(v_1!v_2!)^{N_S}$  corresponds to the indiscernibility factors inside all the  $N_S$  solutes. The two terms, Eqs. 10 and 11, are different. In fact, there are less states in the case we consider global solute instead of individual atoms because the exchange of atoms between clusters is forbidden.

This effect can be modelled thanks to the characteristic function formalism<sup>2-4</sup>. Generalizing the results for a simple dumbbell electrolyte, as described in Ref.<sup>3</sup>, we finally obtain the following expression of the standard chemical potential of any molecular solute

$$\mu_S^\circ = -k_B T \ln z_S, \quad (12)$$

with

$$z_S = \frac{1}{\rho^\circ \prod_i \Lambda_i^{v_i} v_i!} \frac{\int d\mathbf{r}'_S \int d\mathbf{r}^N \exp(-\beta \tilde{V})}{\int d\mathbf{r}^N \exp(-\beta V)}. \quad (13)$$

Here  $\tilde{V}$  is the potential of the system with only one solute at  $\mathbf{r}_S = \mathbf{0}$ . Thus the reference atom is immobile but the other ones can move and their configurational integral is represented by the integrand  $\int d\mathbf{r}'_S$ . Moreover, the potential is  $\tilde{V} = +\infty$  if the coordinates of the atoms are such that they do not belong to the aggregate (because e.g. the atoms are far away). This point actually yields the criterion for the definition of the aggregate (molecular solutes): when do we consider that the atoms correspond to the same molecular solutes? In fact it depends on the choice taken to define microscopically the molecular solute. Following a well-known Onsager statement<sup>5</sup>, the MAL constant (and the activity coefficients) in a chemical reaction depends on the way we microscopically define the species. There is no objective choice. All of them, when calculated rigorously, yield the correct thermodynamic properties of the system, even if of course, for the sake of simplicity we try to consider a criterion with the activity coefficients closest to 1<sup>6</sup>.

Consequently, the standard chemical potential is nothing but the excess free energy of the molecular solute in the solvent (with the standard correction term  $\rho^\circ$ ). The resulting MAL constant (Eq. 3) is nothing but the ratio of the  $z_S$ , i.e.,  $z_C/(z_A z_B)$ . It should be noted that the de Broglie length terms cancelled out. The Gibbs energy of the reaction is the difference of the free energy  $\mu_C^\circ - \mu_B^\circ - \mu_A^\circ$ .

This relation provides a method to calculate  $K^\circ$  by umbrella sampling: we consider the change in free energy when  $B$  comes close to  $A$ . The difference is the integral over

the position of particle  $B$  when it comes close to the reference particle of  $A$ . The limit is the criterion for the definition of the molecular aggregate  $C$ . Thus we finally obtain the generalized Bjerrum formula of association for molecular solutes

$$K^{\circ} = \int_0^{r_{\max}} \exp(-\beta V^{\text{MM}}) 4\pi r^2 dr^2, \quad (14)$$

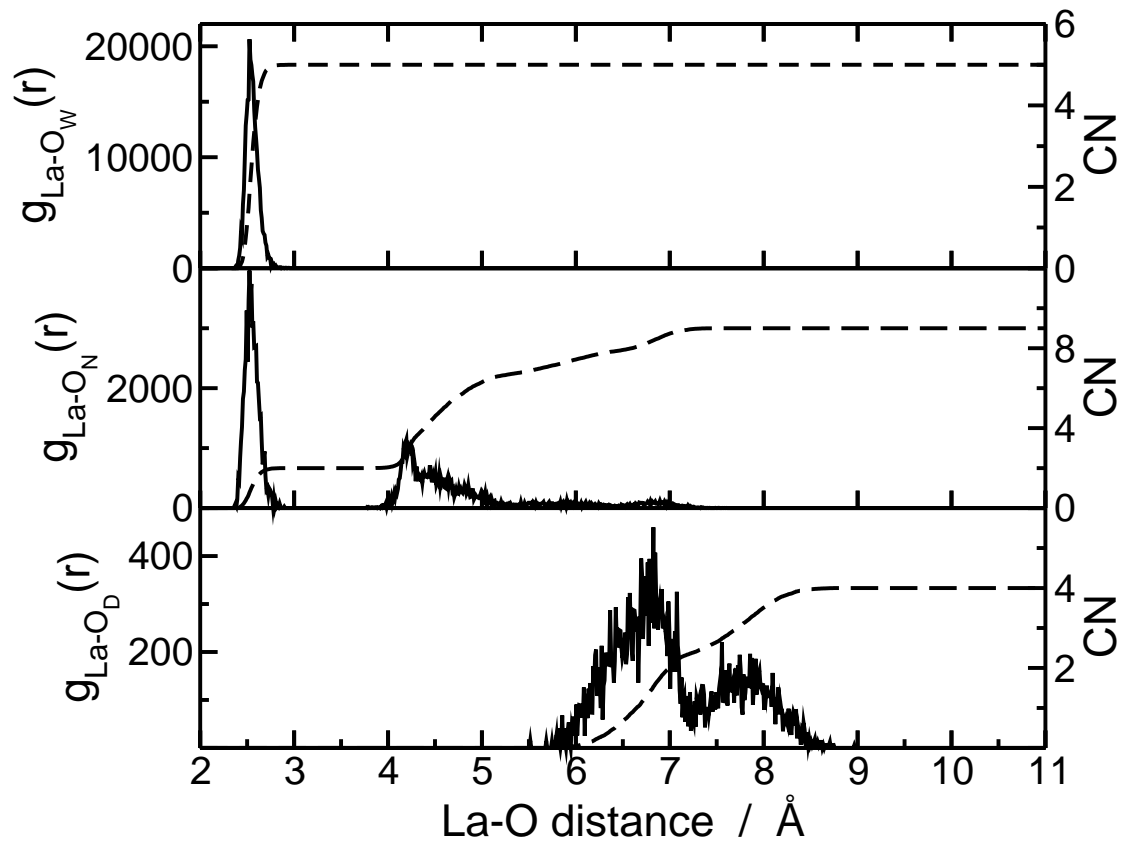
where  $V^{\text{MM}}$  is the McMillan-Mayer (MM) potential that corresponds to the potential calculated by umbrella sampling  $V^{\text{US}}$  corrected with entropic term  $2 \ln r$

$$\beta V_{ij}^{\text{MM}} = \beta V_{ij}^{\text{US}} + 2 \ln r. \quad (15)$$

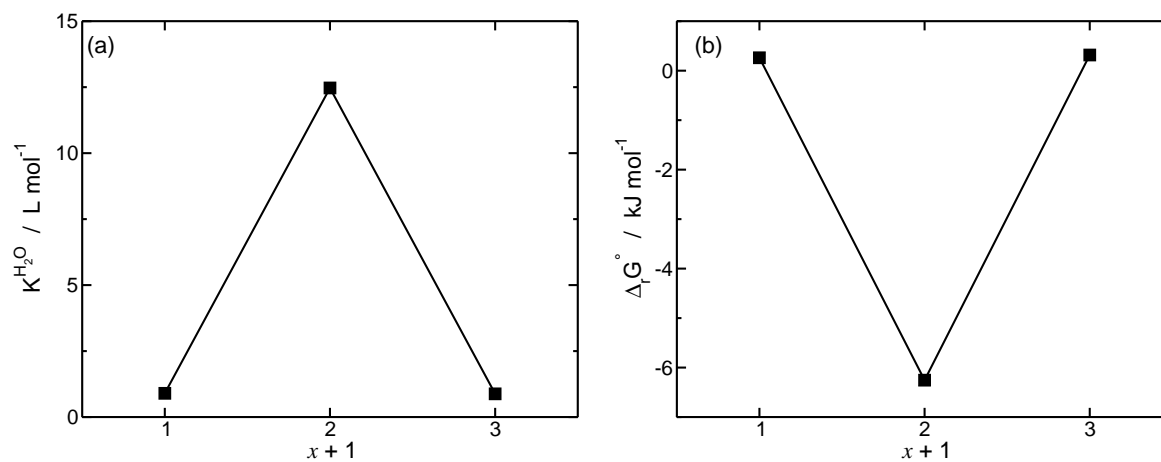
$r_{\max}$  is the distance which defines the associated solute  $A$ . In our case, this distance corresponds to the size of the  $\text{La}^{3+} - \text{OH}_2$  pair and has been taken equals to 12 Å.

In this approach with chemical equilibria between the solutes, the most important approximation is not on the MAL constant but on the activity coefficients, generally neglected. In fact, there are activity coefficients because the solutes  $A$ ,  $B$ , and  $C$  interact with each others. A part of the  $A - B$  interactions is taken into account by the solute  $C$  (up to distance  $r_{\max}$ ), but there are still solute - solute interactions (e.g., the  $A - A$ ,  $B - B$ ,  $C - C$  interactions and the  $A - B$  interactions for  $r > r_{\max}$ ).

## S2 Figures



**Fig. S1**  $\text{La}^{3+}$ -O radial distribution functions (solid line) and corresponding coordination numbers (dashed line) calculated for the  $\text{La}^{3+}$ - $\text{O}_W$  (top),  $\text{La}^{3+}$ - $\text{O}_N$  (middle), and  $\text{La}^{3+}$ - $\text{O}_D$  (bottom) interactions. Note that  $\text{O}_W$ ,  $\text{O}_N$ , and  $\text{O}_D$  correspond to the oxygen atoms of the water molecule, the nitrate anion, and the DMDOHEMA molecules, respectively.



**Fig. S2** (a) Association constant  $K^{\text{H}_2\text{O}}$  and (b) free energy  $\Delta_r G^\circ$  as a function of the number of water molecules in the aggregate  $x$  as defined in Eq. 3 (in the paper) calculated for an aggregate composed of 3 DMDOHEMA molecules.

### S3 Tables

**Table S1**  $K^{\text{H}_2\text{O}}$  and  $\Delta_r G^\circ$  values calculated for the aggregates composed of four and three DMDOHEMA and different numbers of water molecules

	4 DMDOHEMA		3 DMDOHEMA	
	$K^{\text{H}_2\text{O}^a}$	$\Delta_r G^{\circ b}$	$K^{\text{H}_2\text{O}^a}$	$\Delta_r G^{\circ b}$
$A_0 + \text{H}_2\text{O} \rightarrow A_1$	0.2	1.61	0.8	0.11
$A_1 + \text{H}_2\text{O} \rightarrow A_2$	1.7	-0.53	12.5	-2.52
$A_2 + \text{H}_2\text{O} \rightarrow A_3$	7.0	-1.95	0.9	0.13
$A_3 + \text{H}_2\text{O} \rightarrow A_4$	4.8	-1.57		
$A_4 + \text{H}_2\text{O} \rightarrow A_5$	2.0	-0.69		
$A_5 + \text{H}_2\text{O} \rightarrow A_6$	0.1	2.30		

<sup>a</sup> Association constant (in  $\text{L mol}^{-1}$ ). <sup>b</sup> Free energy (in  $\text{kJ mol}^{-1}$ ).

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