


Chemical models for dense solutions

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Here we examine the question of the chemical models widely used to describe dense solutions, particularly ionic solutions. First, a simple macroscopic analysis shows that, in the case of weak interactions, taking into account aggregated species amounts to modelling an effective attraction between solutes, although the stoichiometry used does not necessarily correspond to atomic reality. We then use a rigorous microscopic analysis to explain how, in the very general case, chemical models can be obtained from an atomic physical description. We show that there are no good or bad chemical models as long as we consider exact calculations. To obtain the simplest possible description, it is nevertheless advisable to take the speciation criterion that minimises the excess terms. Molecular simulations show that, very often, species can be defined simply by grouping ions which are in direct contact. In some cases, the appearance of macroscale clusters can be predicted.

1 Introduction

Electrolytes in aqueous solution or in other solvents are modelled differently depending on the concentration regime.

• Firstly, in the case of dilute electrolytes, we generally follow the formalism proposed by Debye, H ckel¹ and Onsager.² Dilution means that long-range effects predominate. It is therefore a regime in which electrostatics is predominant, but as the ions are far apart, it is dominated by thermal agitation and the equations can therefore be linearised, allowing them to be solved. This is the domain of the limiting laws in the square root of the concentration, which control the equilibrium properties (chemical potentials, for example) and transport coefficients (conductivity, diffusion coefficients, viscosity, for example).³ These laws are exact in this limit and are very useful for analytical chemistry, but in practice their range of validity is very small, typically for the concentrations of less than 10^{-1} mol L⁻¹ for the best case, which is that of weakly charged 1–1 electrolytes in a solvent such as water, which has a very high dielectric constant. This area shows that the interaction between ions is mainly attractive, which is rather stabilising for the solution.

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• Then there is the regime of high concentrations, and in particular that of dense media. If we stay around average concentrations, simple extensions of Debye and Hückel laws are possible. The most obvious effect is due to the size of the ions. The purely attractive nature of the Debye–Hückel model is not valid anymore. It is counterbalanced by repulsive forces that increase the chemical potentials, forces that can be described, for example, as steric forces. In this context, the primitive model of electrolytes, in which they are described as charged hard spheres, is of particular interest.^{4–6}

• For the highest concentrations, this description needs to be completed. First of all, the sizes of the ions are not necessarily additive.⁷ There are preferential interaction⁸ effects between ions (generally called Hofmeister's effects) and new specific attractive forces can then appear. At high concentrations, the behaviour of solutions is very different. For some electrolytes, which are highly repulsive, the activity coefficient increases sharply, while for others it remains close to 1 and may even decrease.

The attractive effects at high concentration are often described by a chemical model.^{9–11} It is assumed that ion pairs are formed at high concentrations due to the interaction between cations and anions. This new species¹² significantly reduces the chemical potential and conductivity. It is therefore possible to measure association constants. These association effects often seem to be directly linked to the charge of the ions, the most charged and smallest electrolytes generally being the most associated. In that case, the ion pairs are known as Bjerrum¹³ pairs. Bjerrum proposed the first model to predict these association constants K_{Bj} by assuming a mainly electrostatic interaction occurring from the contact distance σ of the ions:

$$K_{\text{Bj}} = \int_{\sigma}^{r_{\text{max}}} \exp\left(-\frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r r k_B T}\right) 4\pi r^2 dr \quad (1)$$

where $Z_i e$ and $Z_j e$ are the charges of the ions i and j of the pair. $\epsilon_0\epsilon_r$ is the dielectric constant of the solvent. $k_B T$ is thermal energy and r is the distance between the two ions in the pair. The maximum distance is r_{max} . The value of this parameter defines the pair: the ion pair is defined as a cation–anion group situated at a distance less than r_{max} . If the distance is greater, the ions are considered to be free. The choice of this value, and more generally the microscopic criterion chosen to define the pair, is the decisive factor in building a chemical model. There is no general rule, even if we can generally consider that species are formed in configurations where the attractive interaction dominates the thermal energy

$k_B T$. Bjerrum takes $r_{\text{max}} = Z_i Z_j L_B / 2$ where $L_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$ is Bjerrum's length because this distance corresponds to the inflexion point of the ionic distribution. K_{Bj} is the Mass Action Law (MAL) constant where the activity is defined as the number concentration. The dimensionless MAL constant K° is $K^\circ = N_A C^\circ K_{\text{Bj}}$ with N_A the Avogadro constant and C° the molar concentration defining the standard state, generally taken to be 1000 mol m^{-3} . Bjerrum's concept of electrostatic pairs can be generalised to charged interfaces. We can thus define adsorption constants^{14–17} for adsorbed ions, which are of great practical use in predicting surface charge states, and which can be roughly predicted by extending the Bjerrum model to interfaces, as the MUSIC model¹⁸ does, for example.



This shows that Bjerrum's concept of ion pairs is not historically a rigorous one: the interactions are certainly not mainly ionic at short distances and the definition of the pair is problematic. Experimentally, the values measured are not always consistent. They may depend on the quantity under consideration, unlike speciation defined by covalent bonds. It is therefore necessary to question these chemical models¹⁹ for weak interactions such as those between ions in a dense medium.

The most spectacular way of doing this is to use molecular dynamics simulation. For some years now, it has not only been possible to simulate these concentrated solutions, but above all to build chemical models on a molecular basis.^{20–22} In particular, the use of biased simulations makes it possible to calculate the effective interaction between ions, and therefore to calculate chemical speciation more rigorously. Generally, the previous Bjerrum relation (1) is used directly, replacing the Coulomb potential with the effective potential (Potential of Mean Force PMF) calculated by averaging over the solvent configurations.

In a nutshell, generally speaking, chemical models for non-covalent interactions are an extremely common way of modelling complex solutions, since they provide both a chemical microscopic image of the solution and a way of estimating all the thermodynamic quantities. However, despite recent advances in simulation, their justification is not obvious, which makes the interpretation of their results problematic. What do the species modelled in this way really represent?

The purpose of this article is to provide an answer to this question:

- Firstly, we will show how, in all generality and without approximation, a *chemical model* can be defined on the basis of a *physical model* in which only elementary components and their interactions are considered. It will then be shown that chemical species can always be defined in principle, whatever the criteria used to define them. We can then determine the thermodynamic quantities for this chemical model where ions or molecules are possibly formed. At chemical equilibrium, these give exactly the same thermodynamic quantities as the original physical model which does not take these chemical species into account. The results here are quite general and applicable to all types of associating solutes, charged or not, monoatomic or polyatomic, rigid or not, small or large. On the other hand, the proposed method is not necessarily simpler than the original physical model, and in practice can require a numerical solution.

- Finally, we will apply this formalism to the case of simple systems. This will mainly involve describing simple, spherical or roughly spherical ions in bulk or confined aqueous solutions. We will show in which situation these chemical models can claim to represent dense ionic media rigorously in practice.

The central question is how to define chemical species in a concentrated environment controlled by weak interactions. More generally, is it possible to define a species rigorously? Is there a good criterion for defining species? What do multiple associations mean? What is the role of excess terms in speciation?

This article is organised as follows. First of all, we will study macroscopic models of association and their relevance for obtaining thermodynamic quantities in the case of weak interactions. In the following section we propose a rigorous microscopic theory of chemical association in this case. The calculation is quite general and the aim is to deduce a chemical model from an atomic microscopic model. In particular, it will be shown that, in principle, there is no



good or bad association criterion, since they can all give exactly the same physical model. The problem is therefore to choose this criterion *in practice*. We will see in the next section that this is often quite simple at high temperatures, and we will show a few examples. The case of multiple associations typical of concentrated solutions is also discussed. For the sake of simplicity, we will consider mainly the thermodynamic properties. First of all, we will study macroscopic models of association and their relevance for obtaining thermodynamic quantities in the case of weak interactions. In the following section we propose a rigorous microscopic theory of chemical association in this case. The calculation is quite general and the aim is to deduce a chemical model from an atomic microscopic model. In particular, it will be shown that, in principle, there is no good or bad association criterion, since they can all give exactly the same physical model. The problem is therefore to choose this criterion *in practice*.

2 What it means to write a chemical reaction: the macroscopic level

2.1 Writing a chemical reaction is a simple way of modelling attractive forces in concentrated solution... except for electrostatic forces!

Let us first consider the case of a solution where two species A and B can form a pair P. The associated chemical kinetics are assumed to be rapid. There are two ways of looking at the problem thermodynamically:

- First of all, we can make a *physical model* where we only consider the two elementary species A and B, supporting all the forms (free or in pairs). In this case, The Gibbs free energy total differential reads (at constant temperature and pressure)

$$dG_1 = \mu_{A^{\text{tot}}} dn_{A^{\text{tot}}} + \mu_{B^{\text{tot}}} dn_{B^{\text{tot}}} \quad (2)$$

with $\mu_{A^{\text{tot}}}$, $\mu_{B^{\text{tot}}}$, $n_{A^{\text{tot}}}$ and $n_{B^{\text{tot}}}$ the chemical potentials and amounts of substances associated with the two model species A^{tot} and B^{tot} .

- We then have a *chemical model* where we consider three species, the two species A and B when they are free A^{free} and B^{free} , and the pair, P. Using notations similar to the previous eqn (2), we obtain the Gibbs free energy total differential:

$$dG_2 = \mu_{A^{\text{free}}} dn_{A^{\text{free}}} + \mu_{B^{\text{free}}} dn_{B^{\text{free}}} + \mu_P dn_P \quad (3)$$

If chemical equilibrium is reached, it can be shown that the two models are strictly equivalent. Indeed, the MAL is $\mu_P = \mu_{A^{\text{free}}} + \mu_{B^{\text{free}}}$. We also have $n_{A^{\text{tot}}} = n_{A^{\text{free}}} + n_P$ and $n_{B^{\text{tot}}} = n_{B^{\text{free}}} + n_P$ so that

$$dG_2 = \mu_{A^{\text{free}}} dn_{A^{\text{tot}}} + \mu_{B^{\text{free}}} dn_{B^{\text{tot}}} \quad (4)$$

This eqn (4) shows that the two Gibbs energies are formally the same and that the chemical potentials of the species in all forms are equal to the chemical potentials of the free species: $\mu_{A^{\text{tot}}} = \mu_{A^{\text{free}}}$ and $\mu_{B^{\text{tot}}} = \mu_{B^{\text{free}}}$. If we consider that the chemical model with three species is close to ideality, we can deduce that the degree of dissociation α is nothing more than the activity coefficient of the species in the physical model:



$$\alpha = \gamma_{\text{A}}^{\text{tot}} = \gamma_{\text{B}}^{\text{tot}} \quad (5)$$

The pair therefore only decreases the chemical potential of the species because it represents attractive forces. Conversely, attractive forces in solution can often be modelled by the formation of chemical species. As in this case, a complex physical model with activity coefficients can be replaced by a simpler chemical model where the solution is ideal but a pair is formed. Sometimes it is not possible to recover the experimental data over a wide range of concentrations by considering only a single aggregated species, and other species, such as triplets or quadruplets, need to be added.

This is what modellers very often do to represent complex solutions: they add species (pairs, triplets, quadruplets, *etc.*) as a function of concentration to reproduce experimental data as closely as possible over a wide range of concentrations. However, this does not mean that these data necessarily have a microscopic reality.

An important exception to this method is the case of ionic fluids when their equilibrium properties are to be treated rigorously. Since the chemical reactions involve integer numbers of species to form an entity, expansion of the activity coefficient in concentration c cannot have half-integer powers. However, this is required by the Debye–Hückel limiting law for dilute solutions. For example, in the formation of a simple pair, the Mass Action Law (MAL) gives $K^\circ = \frac{(1-\alpha)}{\alpha^2 c}$. The activity coefficient of A or B is thus

$$\gamma = \alpha = 1 - K^\circ c + 2(K^\circ c)^2 + O(c^3) \quad (6)$$

where no $c^{1/2}$ term is present. Consequently, electrostatic forces cannot be treated by a chemical model. Activity coefficients of the Debye–Hückel type must always be retained in chemical models if a rigorous model is to be obtained. This is what coherent models of solutions^{10,23} do when they represent the properties of electrolytes at low and high concentrations. Ebeling's theory of electrostatic association^{24,25} uses a similar strategy. This makes it possible, for example, to obtain an expression for the association constant by identifying the result of the chemical model with that of an expansion of the excess terms. In practice, Ebeling's expression of association constant is similar to that of Bjerrum.

2.2 The stoichiometry of the species can be obtained for the lowest molecularities from measurements at low concentration

Thermodynamic measurements can therefore, at least in principle, provide the value of the equilibrium constants by adjusting the data as a function of concentration. Can they also give the nature of the resulting species? In principle, this is a much trickier problem. In fact, for dilute solutions, it is sufficient to plot the activity of one species as a function of the logarithm of the concentration of another with which it associates. For example, if an ion A binds with a ligand B by a simple chemical reaction $\text{A} + n\text{B} = \text{C}$, the resulting MAL shows that the global activity coefficient of ion A is $\ln \gamma = -\ln K^\circ - n \ln C_{\text{B}}$. The coordination number n can be obtained by plotting $\ln \gamma$ as a function of $\ln C_{\text{B}}$, where C_{B} is the concentration of B.



This is the advantage of the slope method,²⁶ which is widely used to characterise solvent phases during the extraction of metal ions. However, the method is rather tricky to implement, as it often requires considerable dilution for the method to be meaningful when the aim is to characterise concentrated solutions. The method could also be used to characterise the aggregation number of micelles, but in practice the sensitivity is very low and a pseudophase model where the aggregated species are considered as a second liquid phase is generally preferred.

3 What it means to write a chemical reaction: the microscopic level

It is not at first sight very simple to propose a similar method on a microscopic scale. In this case, it is necessary to define an atomic model in which the aggregated chemical species are explicitly present, from another atomic model in which this chemistry is implicit. As before, for the sake of simplicity, the model in which the aggregated species are explicitly considered will be called the *chemical model*, and the model in which this speciation is not distinguished but simply described by interactions will be called the *physical model*. Both models are atomic but with different species. The physical model is the original molecular model, which can be explored by molecular dynamics. The chemical model, on the other hand, is intended to be simplified, *e.g.* by neglecting correlations between species to arrive at a simpler chemical description. We therefore need to transform the partition function of the physical model, which is the simplest because it contains the smallest number of species, into a more complex partition function because it contains more species. The aim of this transformation is to make the two partition functions strictly equivalent.

As we pointed out in the introduction, a central problem is the criterion used to determine the chemical species present. How, for example, can we say that two monoatomic ions are associated? Is it enough to say that they are less than a certain distance apart? And if so, what is the limit value? There are many possible criteria and the recipe for determining the right one is not known. Generally speaking, it can even be said that the right criterion does not exist. Chemistry is not a matter of Nature. It is the observer who, according to their point of view, decides which atoms are associated or not. Chemical species only really exist in the mind (or eyes) of the observer. As pointed out by Onsager²⁷ at the conference in electrochemistry in Montpellier (France) in 1968, when discussing the Bjerrum association model, the definition of a “pair” is completely arbitrary: “The distinction between the free ions and associated pairs depends on an arbitrary convention (...) In a complete theory this would not matter; what we remove from one page of the ledger would be entered elsewhere with the same effect.” Indeed, the aim of this part is to show that all the criteria defining chemistry are in fact possible, at least theoretically. There are an infinite number of possible chemical models, but at chemical equilibrium, they all yield exactly the same physical model, provided that the calculations are carried out exactly. Note that this problem also arises when defining solvent molecules, and more generally when defining any molecule from atoms. However, the choice is much less delicate in the case of molecules linked by covalent bonds than in the case of aggregates formed by weak interactions between solutes, which may be dominated by thermal agitation.



3.1 The golden rule to define chemical potential in statistical thermodynamics

To keep the formulae as general as possible without making them long and unreadable, we will consider here a case where a compound A is formed from ν_1 atoms (or ions) 1 and ν_2 atoms (or ions) 2. Generalization to the case where several associated compounds and/or with more atoms in the compound are present will be immediate. Thus the equilibrium between species reads:

$$\nu_1 1 + \nu_2 2 = A \quad (7)$$

Every point in phase space $\{q, p\}$ corresponds to a given number of A. The criteria for defining species A can be very diverse. Generally they are based on the distances between the atoms. As we have indicated, the choice for defining chemical specificity depends on the modeller and the formalism proposed here must be valid whatever it may be. It just has to be unambiguous, *i.e.* the criterion must allow us to decide, for any configuration of the phase space, the number of species A and the atoms that make them up. The calculation of canonical or grand-canonical partition functions of the physical model involves summing and integrating terms of the form

$$\frac{1}{N_1!N_2!} e^{-\beta H(\{q, p\})} \quad (8)$$

where $H(\{q, p\})$ is the Hamiltonian, $\beta = 1/k_B T$ is the inverse temperature. N_1 and N_2 are the numbers of particles 1 and 2. The aim is to transform this simple term of the physical model (where only 1 and 2 are present) into an equivalent term for the chemical model (where A and free 1 and 2 are present). The term (8) is practically the sum of contributions comprising different states with different numbers of A N_A . There are several possible strategies. We can, for example, introduce the indicator (or characteristic) functions formalism^{22,28} to decompose the phase state. This leads to a hard chemical Hamiltonian $\tilde{H}(\{q, p\})$ which is equal to $H(\{q, p\})$ if the point in phase space has the correct number of A's and equal to $+\infty$ if this is not the case.

To simplify the calculation, we take another route and define an ordered chemical Hamiltonian $\tilde{H}(N_A, \{q, p\})$. It is only equal to the Hamiltonian $H(\{q, p\})$ if not only is N_A correct, but also the particles are well ordered. The first compound A must thus be made up of the first ν_1 atoms (or ions) 1 and the first ν_2 atoms (or ions) 2, the second compound A is made up of the next ν_1 atoms (or ions) 1 and the next ν_2 atoms (or ions) 2, and so on. If the point in the phase space $\{q, p\}$ does not verify this, then $\tilde{H}(N_A, \{q, p\}) = +\infty$. The term for partition functions (8) thus becomes:

$$\sum_{N_A} \mathcal{N}(N_A) \frac{1}{N_1!N_2!} e^{-\beta \tilde{H}(N_A, \{q, p\})}. \quad (9)$$

$\mathcal{N}(N_A)$ is a combinatorial term equal to the number of ways of choosing the N_A compounds A and putting them in order:

$$\begin{aligned} \mathcal{N}(N_A) = & \frac{1}{N_A!} \binom{N_1}{\nu_1} \binom{N_1 - \nu_1}{\nu_1} \dots \binom{N_1 - (N_A - 1)\nu_1}{\nu_1} \binom{N_2}{\nu_2} \\ & \times \binom{N_2 - \nu_2}{\nu_2} \dots \binom{N_2 - (N_A - 1)\nu_2}{\nu_2} \end{aligned} \quad (10)$$



The expression is divided by $N_A!$ because in the chemical Hamiltonian $\tilde{H}(N_A, q, p)$, the order of the aggregates is irrelevant: if we exchange two of them, they correspond to the same state in the original physical Hamiltonian $H(\{q, p\})$. We obtain:

$$\mathcal{N}(N_A) = \frac{N_1!N_2!}{\nu_1!N_A\nu_2!N_A(N_1 - N_A\nu_1)!(N_2 - N_A\nu_2)!N_A!} \quad (11)$$

We thus find the indistinguishability factors of the chemical model which explicitly takes A into account. $N_1 - N_A\nu_1 = N_1^f$ is the number of free particles 1 and $N_2 - N_A\nu_2 = N_2^f$ is the number of free particles 2. The term for the partition function (8) is therefore

$$\frac{1}{N_1!N_2!}e^{-\beta H(\{q,p\})} = \sum_{N_A} \frac{1}{N_1^f!N_2^f!N_A!\nu_1!N_A\nu_2!N_A!}e^{-\beta \tilde{H}(N_A, \{q,p\})}. \quad (12)$$

Thus the expression can be easily generalized for the cases where the speciation involves more than two species α in the aggregate A

$$\sum_{\alpha} \nu_{\alpha} \alpha = A \quad (13)$$

In that case, (12) becomes

$$\frac{1}{\prod_{\alpha} N_{\alpha}!}e^{-\beta H(\{q,p\})} = \sum_{N_A} \frac{1}{N_A! \prod_{\alpha} N_{\alpha}^f! \left(\prod_{\alpha} \nu_{\alpha}! \right)^{N_A}} e^{-\beta \tilde{H}(N_A, \{q,p\})}. \quad (14)$$

This makes it easy to link the two physical and chemical models. The term of the partition function of the chemical model (14) is the expected one with, for example, the indistinguishability factor $N_A! \prod_{\alpha} N_{\alpha}^f!$. However, there are three important points to make this link.

- A sum over all possible chemical species distributions is necessary. This means that the two models can only be equivalent if they are averaged over all possible chemistry, as in the grand canonical ensemble. This brings us back to the idea that the physical and chemical models are only equivalent at chemical equilibrium.

- The chemical Hamiltonian $\tilde{H}(N_A, \{q, p\})$ is a hard Hamiltonian. In practice, its definition is very simple: it is exactly the physical Hamiltonian $H(\{q, p\})$ as long as the configuration respects the correct chemistry, and it is equal to $+\infty$ if it is not the case.

- Internal indistinguishability factors $\prod_{\alpha} \nu_{\alpha}!$ must also be taken into account. They correspond to the possible exchanges of identical particles in the aggregates which do not modify the number of microstates if the particles α are assumed to be indistinguishable.

The previous formula can be directly extended to the general case where several chemical species can be formed. In this case, we obtain:

$$\frac{1}{\prod_{\alpha} N_{\alpha}!}e^{-\beta H(\{q,p\})} = \sum_{\chi} \frac{1}{\prod_c N_c^{\chi}! \left(\prod_{\alpha} \nu_{\alpha}^c! \right)^{N_c}} e^{-\beta \tilde{H}(\chi, \{q,p\})}. \quad (15)$$

χ represents all the distributions of possible chemical species c which are either free species or aggregates. N_c^{χ} is the number of c in the configuration χ and ν_{α}^c is



the number of atoms (or ions) α in the chemical species c . A chemical model, whatever the criterion under consideration, can be obtained from the physical model. This eqn (15) links the partition functions of the chemical and physical models in all situations. It thus allows the thermodynamic variables of the chemical model to be rigorously defined at the microscopic level, which in turn allows a macroscopic chemical model to be obtained. This is the most important result of this article.

3.2 Chemical equilibria

In the grand-canonical ensemble, the grand partition function calculated using eqn (14) reads

$$\sum_{\{N_\alpha\}} \int \frac{dq dp}{h^{3N_{\text{tot}}}} \prod_{\alpha} \frac{e^{N_{\alpha} \beta \mu_{\alpha}}}{N_{\alpha}!} e^{-\beta H(\{q,p\})} = \sum_{\{N_{\alpha}^f\}, N_A} \int \frac{dq dp}{h^{3N_{\text{tot}}}} \frac{\left(\frac{e^{\sum_{\alpha} \nu_{\alpha} \beta \mu_{\alpha}}}{\prod_{\alpha} \nu_{\alpha}!} \right)^{N_A}}{N_A!} \prod_{\alpha} \frac{e^{N_{\alpha}^f \beta \mu_{\alpha}}}{N_{\alpha}^f!} e^{-\beta \tilde{H}(N_A, \{q,p\})} \quad (16)$$

Thus the grand potential of the chemical model is identical to that of the physical model if the chemical potentials of the free atoms (or ions) μ_{α}^f are equal to the chemical potentials of these atoms in the physical model and if

$$\mu_A = \sum_{\alpha} (\nu_{\alpha} \mu_{\alpha} - k_B T \ln \nu_{\alpha}!) \quad (17)$$

is satisfied. This equation corresponds to the chemical equilibrium (MAL). The second term $\sum_{\alpha} -k_B T \ln \nu_{\alpha}! = -k_B T \ln \prod_{\alpha} \nu_{\alpha}!$ is an internal exchange entropic term that can be included in the standard chemical potential of the aggregate A to recover the standard MAL $\tilde{\mu}_A = \sum_{\alpha} \nu_{\alpha} \mu_{\alpha}$.

The two models, physical, with no chemical species, and chemical, where the chemical species A is explicitly considered, are therefore strictly equivalent at chemical equilibrium. We have therefore demonstrated Onsager's assertion: there is no good or bad chemical model as long as we make exact calculations in statistical thermodynamics, since they all give the same properties at equilibrium. We just have to remember that in the chemical model the Hamiltonian is the hard chemical Hamiltonian \tilde{H} and that we have to consider an additional entropy term for the chemical potential of the chemical species A $\tilde{\mu}_A$.

$$\tilde{\mu}_A = \mu_A + \sum_{\alpha} k_B T \ln \nu_{\alpha}! \quad (18)$$

All this can be generalized directly to the general case with several chemical species formed, represented by the relation (15).

3.3 Equilibrium constants

The equilibrium constants depend on the convention defining the standard state under consideration. They are related to the standard chemical potentials μ_i° of the various species i involved in the chemical equilibrium. So the problem is to evaluate the latter quantity.



3.3.1 Gas phase. For a gas i , it corresponds to the situation where it is diluted, so only intra-molecular interactions need be taken into account. The canonical partition function of N_i molecules i in a volume V is in that case:

$$Q_{N_i}(T, V) = \frac{1}{N_i! h^{3N_i} \sum_{\alpha} N_{\alpha}} \int dq dp e^{-\beta \tilde{H}(N_i, \{q, p\})} \quad (19)$$

In the limit where the gas is diluted, only the correlations internal to the molecule need be taken into account. If we also assume that the criterion defining chemistry depends only on distances, we can integrate the part depending on the conjugate momenta. We obtain:

$$Q_{N_i}(T, V) = \frac{V^{N_i}}{N_i! \prod_{\alpha} A_{\alpha}^{3N_{\alpha} \nu_{\alpha}}} \left(\int dq_{\text{int}} e^{-\beta \tilde{v}(\{q_{\text{int}}\})} \right)^{N_i} \quad (20)$$

A_{α} is the thermal de Broglie's length of α . $\{q_{\text{int}}\}$ represents the internal degrees of freedom of a molecule. More precisely, this can be, for example, the positions of all the atoms in the molecule except 1, the integration of the position of this reference atom giving the volume term V^{N_i} . $\tilde{v}(\{q_{\text{int}}\})$ is the potential energy as a function of the internal degrees of freedom. The associated free energy $F = -k_B T \ln Q_{N_i}(T, V)$ leads to the chemical potential

$$\mu_i = k_B T \ln \frac{N_i \prod_{\alpha} A_{\alpha}^{3\nu_{\alpha}}}{Z_{\text{int}} V} \quad (21)$$

Z_{int} is the internal partition function:

$$Z_{\text{int}} = \int dq_{\text{int}} e^{-\beta \tilde{v}(\{q_{\text{int}}\})} \quad (22)$$

The standard chemical potential μ_i° is defined from the limiting law:

$$\mu_i = \mu_i^{\circ} + k_B T \ln \frac{N_i k_B T}{P^{\circ} V} \quad (23)$$

so that

$$\mu_i^{\circ} = k_B T \ln \frac{P^{\circ} \prod_{\alpha} A_{\alpha}^{3\nu_{\alpha}}}{Z_{\text{int}} k_B T} \quad (24)$$

The internal entropy term $\sum_{\alpha} k_B T \ln \nu_{\alpha}!$ must be added to this term to obtain the true chemical potential:

$$\tilde{\mu}_i^{\circ} = k_B T \ln \frac{P^{\circ} \prod_{\alpha} A_{\alpha}^{3\nu_{\alpha}}}{Z_{\text{int}} k_B T} \quad (25)$$

where the internal partition function of the molecule takes into account the entropic indistinguishability factor:

$$\tilde{Z}_{\text{int}} = \frac{1}{\prod_{\alpha} \nu_{\alpha}!} \int dq_{\text{int}} e^{-\beta \tilde{v}(\{q_{\text{int}}\})} \quad (26)$$

The standard chemical potentials, and therefore the equilibrium constants, are directly related to the internal correlations of the different species involved in



the reaction. In practice, the de Broglie length terms do not affect the equilibrium constant and can be omitted. In fact, due to the conservation of matter, they appear in the same quantities on the reactants and products of the reaction and their effect is cancelled out. For example, for a chemical reaction between two atoms, $1 + 2 = 3$, we get $\tilde{\mu}_1^\circ = k_B T \ln \frac{P^\circ \Lambda_1^3}{k_B T}$, $\tilde{\mu}_2^\circ = k_B T \ln \frac{P^\circ \Lambda_2^3}{k_B T}$, and $\tilde{\mu}_3^\circ = k_B T \ln \frac{P^\circ \Lambda_1^3 \Lambda_2^3}{\tilde{Z}_{\text{int}} k_B T}$. We obtain

$$K^\circ = \frac{P^\circ}{k_B T} \tilde{Z}_{\text{int}} \quad (27)$$

The internal partition function of the molecule can easily be integrated:

$$\tilde{Z}_{\text{int}} = \int e^{-\beta \tilde{v}(r)} 4\pi r^2 dr \quad (28)$$

If two atoms 1 and 2 are the same, the result is formally the same, except that this integral must be multiplied by 1/2.

3.3.2 Solution. The previous calculation makes it easier to understand what happens when calculating equilibrium constants involving solutes in a solution. In this case, the limiting law considered is that associated with Henry's law: the solutes are considered diluted in a pure solvent and no longer in vacuum. It should be noted that the previous calculation in the grand canonical ensemble (16) is still valid, but there is also the solvent. The framework of chemical models in solution is therefore particularly simple when the chemical potential of the solvent is imposed. This framework corresponds to that of the McMillan–Mayer theory^{29,30} of solutions, where the properties of the solute are obtained by averaging over the configurations of the solvent. The calculations are therefore carried out naturally in the grand canonical ensemble.²² This is particularly important for activity coefficients, which can be calculated in this way, but for equilibrium constants, as we are focusing on dilute solutions, we can simplify by considering the canonical ensemble.

Let us start with a point solute, made up of a single atom. Neglecting edge effects, when the solute is sufficiently dilute, the ratio of the canonical partition function of the solution by the one of pure solvent is

$$\frac{Q}{Q_w} = \frac{V^{N_s}}{\Lambda_s^{3N_s} N_s!} \left(\frac{\int dq_w^{N_w} \exp(-\beta \nu^1)}{\int dq_w^{N_w} \exp(-\beta \nu^0)} \right)^{N_s} \quad (29)$$

N_w and N_s are the number of solvent and solute particle, V is the volume and Λ_s is the solute de Broglie's length. ν^1 is the potential energy of the solution when only one solute particle is localized at the origin of the coordinate system and ν^0 is the potential energy of the pure solvent (without solute particles). Then the resulting Helmholtz free energy $F = -k_B T \ln Q$ yields $\mu_s = \mu_s^\circ + k_B T \ln C_s / C^\circ$ where C_s is the molar concentration of the solute. The standard chemical potential of the solute is

$$\mu_s^\circ = k_B T \ln (\Lambda_s^3 C^\circ N_A) - k_B T \ln \left(\frac{\int dq_w^{N_w} \exp(-\beta \nu^1)}{\int dq_w^{N_w} \exp(-\beta \nu^0)} \right). \quad (30)$$

N_A is Avogadro constant. The second term of eqn (30) is nothing but the difference of the free energy of the solvent molecules interacting with one single immobile solute particle at the origin and the free energy of the pure solvent without any



solute particles in the same thermodynamic conditions. The later definition of μ_i° is also valid when the solvent is a mixture of molecules as can be shown by a trivial generalization of this calculation. Consequently eqn (30) is the general expression of the standard chemical potential of a point solute in a solvent.

If the solute is made up of several atoms or ions α , the Hamiltonian of the chemical model must be considered for the partition function. The relationship (29) becomes:

$$\frac{Q}{Q_w} = \frac{V^{N_s}}{\left(\prod_{\alpha} A_{\alpha}^{v_{\alpha}}\right)^{3N_s} N_s!} \left(\frac{\int dq_{\text{int}} dq_w^{N_w} \exp(-\beta v^1)}{\int dq_w^{N_w} \exp(-\beta v^0)} \right)^{N_s} \quad (31)$$

As before, q_{int} represents the internal degrees of freedom of a molecule. The resulting standard chemical potential is

$$\mu_s^\circ = k_B T \ln \left(C^\circ N_A \prod_{\alpha} A_{\alpha}^{3v_{\alpha}} \right) - k_B T \ln \left(\frac{\int dq_{\text{int}} dq_w^{N_w} \exp(-\beta v^1)}{\int dq_w^{N_w} \exp(-\beta v^0)} \right). \quad (32)$$

The function

$$\tilde{v}(\{q_{\text{int}}\}) = -k_B T \ln \left(\frac{\int dq_w^{N_w} \exp(-\beta v^1)}{\int dq_w^{N_w} \exp(-\beta v^0)} \right) \quad (33)$$

is nothing but the difference of the free energy of the solvent molecules interacting with one solute at the origin (with internal degrees of freedom $\{q_{\text{int}}\}$) F_w^1 and the free energy of the pure solvent without any solute particles in the same thermodynamic conditions F_w^* . It therefore corresponds to the potential of mean force between the solute particles averaged over the positions of the solvent when the solutes are infinitely dilute (there is only one solute here). Consequently, this term is nothing but the McMillan–Mayer potential between the α solute molecules. By adding the internal entropic indistinguishability factor we finally obtain:

$$\mu_s^\circ = k_B T \ln \left(\frac{C^\circ N_A \prod_{\alpha} A_{\alpha}^{3v_{\alpha}}}{\tilde{Z}_{\text{int}}} \right) \quad (34)$$

where the internal partition function reads:

$$\tilde{Z}_{\text{int}} = \frac{1}{\prod_{\alpha} v_{\alpha}!} \int dq_{\text{int}} e^{-\beta \tilde{v}(\{q_{\text{int}}\})} \quad (35)$$

This last term is formally the same as in the case of gases, but the potential is now the potential averaged over the solvent configurations (McMillan–Mayer potential).

As before, the equilibrium constant for any reaction can be obtained from these expressions for the standard chemical potentials. Here again, the result does not depend on the de Broglie's lengths, but it may depend on the choice of standard state (C°), depending on the reaction. For a reaction between two monoatomic ions in solution, we obtain as above

$$K^\circ = C^\circ N_A \tilde{Z}_{\text{int}} \quad (36)$$



The internal partition function is given by eqn (28) where $\tilde{v}(r)$ is the McMillan–Mayer potential between the two ions. This relationship corresponds precisely to the Bjerrum’s relationship. Once again, if the two ions are the same, divide \tilde{Z}_{int} by 2.

4 Results and discussion

4.1 What criteria should be used to define chemical species?

The calculation of association constants in solution is therefore possible by thermodynamic integration if we calculate the effective McMillan–Mayer potential between the solutes. To establish a complete chemical model, it is also necessary to calculate the activity coefficients between the solutes, which can be done by the usual methods of liquid physics.³¹ Nevertheless, an important issue is the choice of the criterion to define the chemical species. The formalism we derived is quite general and exact. It can be used for any criterion, but in itself it is of no use because the associated model is no simpler than the initial model: there are more species present and the associated free energy is therefore more complex because it depends on more parameters.

If we consider a simple association between two ions, the criterion is often to consider that the pair is defined when the two ions are at a distance less than a certain limiting distance d . But which d should we take? Bjerrum’s choice ($d = Z_i Z_j L_B/2$) consists in considering the inflection point in the coordination number curve as a function of the distance between the two ions when the McMillan–Mayer potential is supposed to be purely coulombic. Criteria based on coordination numbers are very popular to distinguish solvation layers, but there is no guarantee that the resulting activity coefficients are weak. Another criterion for the choice of d is such that at low concentration, the free energy of the chemical model is equivalent to that of the physical model. This is the strategy proposed by Ebeling.²⁴ For a simple neutral solute, at low solute density ρ the (osmotic)

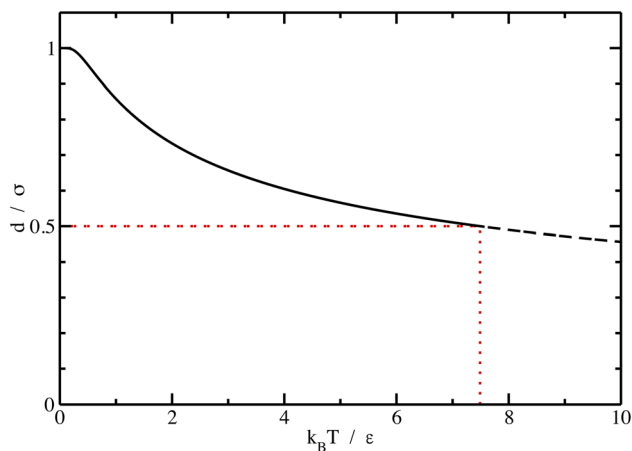


Fig. 1 Maximum distance defining the pair d distance in units of range of potential σ as a function of temperature in reduced units $k_B T / \epsilon$ for a square-well potential. If T exceeds a certain value, d is too small because it should be smaller than the size of the hard core δ . The limit point (in red) is drawn for $\delta = \sigma/2$.



pressure P can be calculated either from the second virial coefficient or from the chemical model:

$$\frac{\beta P}{\rho} = 1 - \frac{\rho}{2} \int_0^{+\infty} \left(e^{-\beta \tilde{v}(r)} - 1 \right) 4\pi r^2 dr = 1 - \frac{\rho}{2} \int_0^d e^{-\beta \tilde{v}(r)} 4\pi r^2 dr \quad (37)$$

This allows d to be defined from the implicit relation:

$$\frac{4}{3} \pi d^3 = \int_d^{+\infty} \left(e^{-\beta \tilde{v}(r)} - 1 \right) 4\pi r^2 dr \quad (38)$$

Note that the value of d does not depend on the effective potential $\tilde{v}(r)$ for distances $r < d$ corresponding to internal correlations within the pair. This brings us back to the idea that the criterion defining the chemical species is defined in order to minimise the activity coefficients which depend in the chemical model on the interactions for $d > r$.

We can see what happens to a square-well potential. In that case, we have a solute for which $\tilde{v}(r) = +\infty$ for $r < \delta$, $\tilde{v}(r) = -\epsilon$ for $\delta < r < \sigma$ and $\tilde{v}(r) = 0$ for $r > \sigma$. At low temperature, $d > \delta$ and we obtain:

$$d = \left(1 - e^{-\frac{\epsilon}{k_B T}} \right)^{\frac{1}{3}} \sigma \quad (39)$$

The curve is plotted in Fig. 1.

For low temperatures ($k_B T < \epsilon$), the size of the pair d corresponds to σ . The pair is thus unambiguously defined and corresponds to pairs of molecules with an association energy of $-\epsilon$. If T increases, d gradually decreases. In an exact model, we could keep the $d = \sigma$ criterion, but if we want to neglect the activity coefficients, it is no longer valid. The system is effectively less attractive. When the temperature reaches $k_B T = -\frac{\epsilon}{\ln\left(1 - \frac{\delta^3}{\sigma^3}\right)}$, $d = \delta$. Thermal agitation is

sufficient to completely compensate for the attraction and there is no need to consider pairs. This corresponds to the temperature where the second virial coefficient is zero. Beyond that, no chemical model without activity correction is possible. Overall, the solutes repel each other by contact forces, with thermal agitation completely dominating attraction. A chemical model can be retained but activity coefficients greater than 1 must be introduced to take account of this predominant physical effect. In this case, the chemical model may be useful for characterising solute pairs in the attractive domain, but it does not simplify the estimation of thermodynamic properties.

This analysis cannot be used directly for charged solutions. The formula (38) cannot be used because the second virial coefficient diverges and another density expansion has to be considered, with a mandatory Debye-Hückel term. Nevertheless, the fact that association constants are well defined at low temperature (or for high charge) where thermal agitation is not enough to overcome attraction is still important.

4.2 Association from molecular descriptions

An important point is that the McMillan-Mayer potential in solution is complex because it reflects the molecular nature of the solvent. Even for single ions, it is



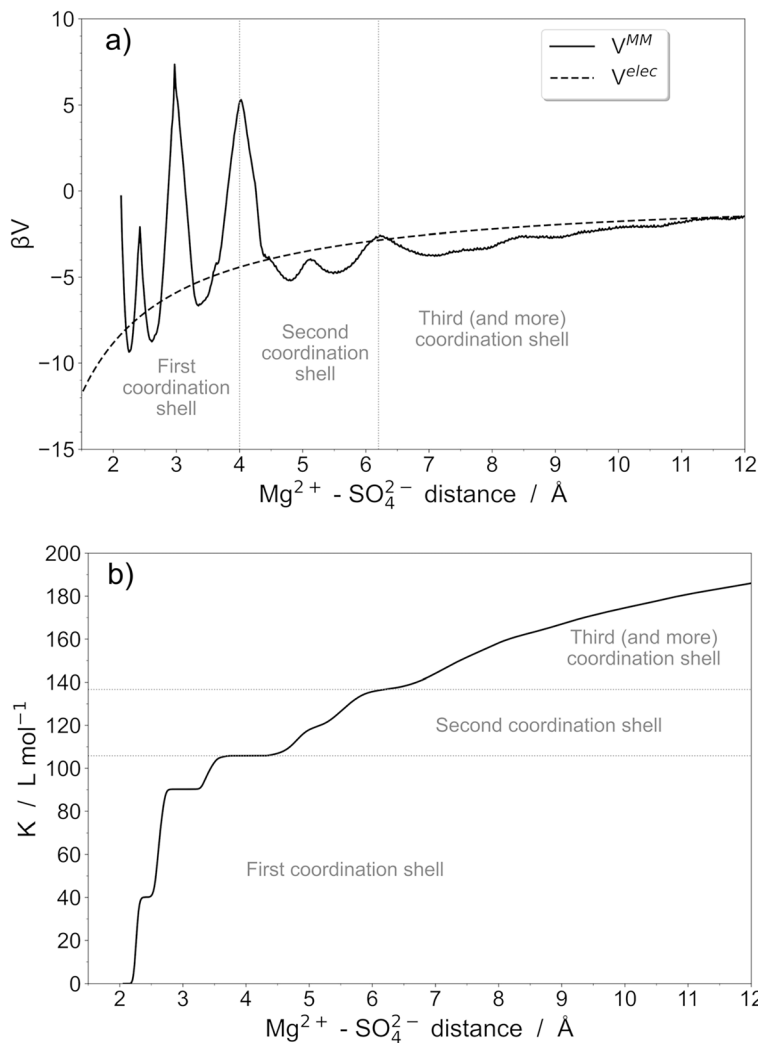


Fig. 2 (a) $\text{Mg}^{2+}-\text{SO}_4^{2-}$ McMillan–Mayer potential (solid line) and corresponding electrostatic potentials (dashed line), and (b) association constant as a function of the $\text{Mg}^{2+}-\text{SO}_4^{2-}$ distance calculated from the MM potentials (solid line). Values of association constants corresponding to different coordination shells are also shown (dotted line).

often not monotonic. In fact, the predominant association is often the formation of Contact Ion Pairs (CIP) in the system. In a CIP, there are no solvent molecules between the two ions and the interaction is often very strong.

As an example, we focus now on the description of the MgSO_4 pair in water by performing explicit polarization molecular dynamics simulations. The effective McMillan–Mayer potential is calculated from the free energy profile associated with the interaction between Mg^{2+} and SO_4^{2-} ions (Fig. 2). This quantity has been calculated using umbrella sampling simulations. Molecular dynamics simulations were performed using Sander10, a module of Amber10,³² using explicit polarization in the *NVT* ensemble. Water molecules were described using the



polarizable rigid water model POL3,^{33,34} while polarizable force fields of Mg^{2+} and SO_4^{2-} were the ones developed in ref. 35.

For the umbrella sampling simulations, we defined the distance between Mg^{2+} and the sulfur atom of SO_4^{2-} ions as the equilibrium reaction coordinate, ranging from 1 to 12 Å with a step size of 0.5 Å. A harmonic restraining force constant of 2 kcal mol⁻¹ Å⁻² was applied. To overcome activation barriers located at approximately 3.2 Å (transition from bidentate to monodentate configurations) and 4.0 Å (transition from the first to the second coordination shell), a constant force of 50 kcal mol⁻¹ Å⁻² was applied. Umbrella sampling simulations were conducted in a simulation box containing 1001 water molecules (31 × 31 × 31 Å³). Production runs were collected for 1 ns. The umbrella sampling simulation protocols were optimized to ensure sufficient overlap of equilibrium windows, ensuring accurate representation of reaction pathways. Free energy profiles were then calculated using the Weighted Histogram Analysis Method^{36–39} (WHAM).

The potential can therefore exhibit marked oscillations around the coulombic curve, reflecting different kinds of ion pairs. Several shells (at least two) can be distinguished but they are divided into well-defined domains that correspond to different coordination modes. We can therefore propose a global model or, in contrast, a model with several types of pairs. If we stop at the CIP, the value of K° is close to 110 and reaches 140 if we take the second shell, which is also strongly associated.

The choice of chemistry depends on how it will be used, but globally for ions it has to be coupled to the way the electrostatic potential is modelled. Numerous macroscopic theories, such as the Mean Spherical Approximation⁴⁰ generalise the Debye–Hückel approach and they are valid only at high temperature. These theories cannot describe the strong electrostatic attractions and they must be modified by considering, for example, the pair explicitly.^{41–44} In that case, the criterion can be obtained by comparing the potential depth to $k_B T$. When compared with experimental data⁴⁵ for transport properties, the important point is the lifespan of species, which should diffuse together. Thus, the comparison with $k_B T$ also makes sense, but we must also look at the activation energy barriers when they are significant.

Chemical association is also important for confined solutions. In particular, in the case of surfaces, recent studies have shown that the important point in describing electrical double layers (EDL), when simple models based on the Poisson–Boltzmann equation are no longer valid, is to take into account a Stern layer made up of ions specifically bonded to the surface. This gives us ion pairs in contact comprising a charged atom of the surface and an ion of opposite charge. This association can also be calculated from molecular dynamics from the same method. For silica surfaces, cations are generally associated to negatively charged oxygen atoms of the surfaces (silanolate groups). The McMillan–Mayer potential can also be calculated. We show here the case of two free energy profiles of lanthanides interacting with a negatively charged silica surface. We use a classical simulation, with LAMMPS. The system and the method⁴⁶ has been originally derived for divalent cations. The methodology has been adapted to lanthanide potentials.⁴⁷ The potential of mean force is determined from Umbrella Sampling using the WHAM algorithm.

Overall, the profiles presented in Fig. 3 are no different from those of single ions in solution. There are fewer coordination modes than for the MgSO_4 pair



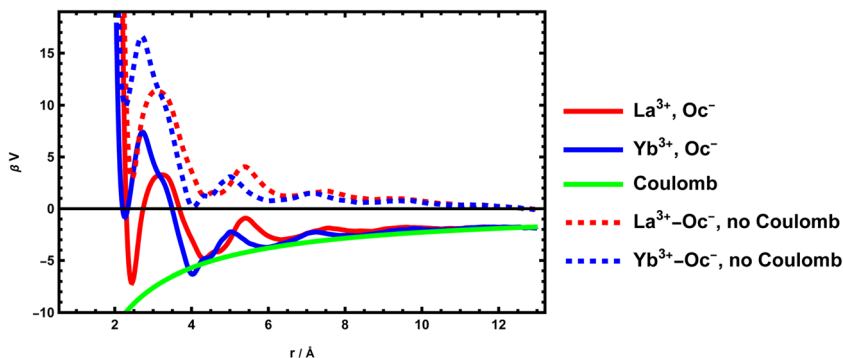


Fig. 3 Effective potential between a charged oxygen atom of the surface of an amorphous silica layer and lanthanide ions in the surrounding aqueous solution for La^{3+} (red) and Yb^{3+} (blue). The dotted line is the same potential when the coulombic part is removed.

because the anion is not molecular. We still mainly find the presence of this CIP around $r = 2 \text{ \AA}$. The value of the constant is trickier to calculate here because it depends on the model that considers it. In EDL, generally, the long-ranged electrostatic force is considered in a non-local way, by solving the Poisson equation. The MAL defining the pairs associated with the surface are therefore defined using not the global chemical potentials but the local electrochemical potentials, which treat the electrostatic term separately. The free ions are therefore assumed to have the same potential as those associated. The coulombic contribution of the McMillan–Mayer potential must therefore be removed to calculate the association constants on a charged surface.

Despite their similarities, the two lanthanide cations have very different adsorption intensities, La^{3+} being less bound than Yb^{3+} . In terms of adsorption constant, we obtain $10^{-3.72}$ for La^{3+} and $10^{-6.75}$ for Yb^{3+} . In terms of Gibbs energy difference, which represents the specificity of the site, it corresponds to a difference of $7 k_{\text{B}}T \approx 17 \text{ kJ mol}^{-1}$ which is important. An important point to note here is that the ratio of constants (or the difference in Gibbs energies) are more important than the absolute values of the constants, as they are entirely modulated by the electrostatic potential, which can vary greatly at the surface. The phenomenon is in fact controlled by the surface charge.

4.3 Multiple associations

Highly concentrated solutions combine ionic associations and it is therefore possible to form contact ion chains⁴⁸ of very large size. For concentrated solutions, this results in large clusters, sometimes called prenucleation clusters^{49,50} if they are formed just before saturation of the electrolyte. In fact, this phenomenon is not necessarily related to the insolubility of the salt. The electrostatic association itself can form these very large polyionic species. This can be understood using a simple model.

Let us assume that the formation of these species is linear and that these aggregates are therefore sequences of CIPs. The smallest aggregate is the classical ion pair for which the association constant K° is given by (36) for atomic ions. When larger species are formed, other ions are added in an alternating sequence



of cations and anions. Species with an even number of ions are unique. To simplify, we assume that each ion can place itself on either side of the chain in configurations similar to those it would have in a simple pair, but divided into two parts (on the left and right of the chain). Thus, for an even chain of size $2n$, the configuration integral of the internal partition functions (35) is $K^{\circ 2n-1}$ and the formation constant is $\frac{K^{\circ 2n-1}}{n!^2}$. For aggregates with an odd number of ions $2n + 1$, there are two symmetrical possibilities: either with an excess cation or an anion.

The two formation constants are the same: $\frac{K^{\circ 2n}}{n!(n+1)!}$. The total number of cations (or anions) in solution C^{tot} is expressed as a function of the concentration of free cations (or anions):

$$C^{\text{tot}} = C + \sum_{n=1}^{+\infty} \left(\frac{nK^{\circ 2n-1}}{n!^2} C^{2n} + \frac{nK^{\circ 2n}}{n!(n+1)!} C^{2n+1} + \frac{(n+1)K^{\circ 2n}}{n!(n+1)!} C^{2n+1} \right) \quad (40)$$

We can then recognise the expansion of the modified Bessel functions of the first kind $I_\alpha(x)$:

$$C^{\text{tot}} = 2CI_0(2K^{\circ}C) + \left(C - \frac{1}{K^{\circ}} \right) I_1(2K^{\circ}C) \quad (41)$$

The average size of clusters can also be calculated from the same method. The results are shown in Fig. 4. In the end, the results are visually quite similar to the formation of micelles.⁵¹ At low concentrations, all the ions are free, but above a certain critical concentration $1/K^{\circ}$, association appears. The difference is that not just one type of aggregate is formed, but a whole succession of states. In the example given here, the increase in size is limited because a chain model offers few connections. But in a globular model, the situation would be very different. In this case the ions have many adsorption sites when they aggregate; typically the constants are multiplied by a factor of $n!$. Then the average size is typically

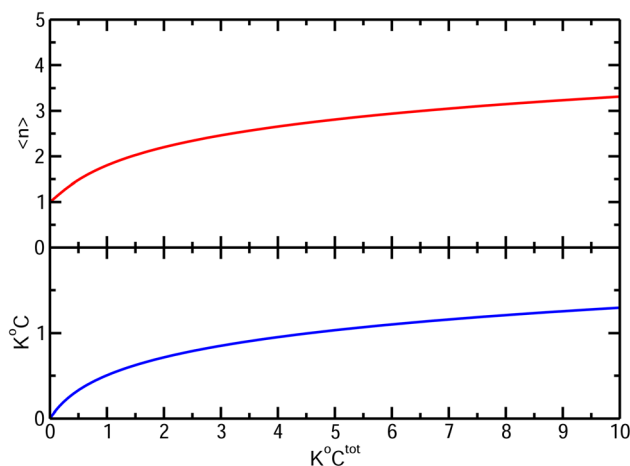


Fig. 4 Bottom: Free ion (either cation or anion) concentration C and Top: average cluster size, as functions of $K^{\circ}C^{\text{tot}}$.



$\langle n \rangle = \frac{1 + K^\circ}{1 - K^\circ}$. It diverges at the critical concentration $1/K^\circ$. Thus for numerous electrolytes, a second regime with a percolation cluster appears above a critical concentration.

In this case, this macroscopic species must be treated separately because it is unique, but this does not necessarily mean that a phase separation occurs. It is simply a sign that we have a true mixture: at high concentrations, statistically all the solutes are in contact and a macroscopic species is bound to form. An attractive interaction can accelerate this percolation phenomenon without inducing a phase transition as has recently been seen⁵² for the solvent phases in liquid–liquid extraction.

5 Conclusion

In this article, we explained how the chemical models used in concentrated, mainly ionic, solutions can be justified. In practice, for weak interactions, these models express an effective attraction between solutes. They can therefore describe macroscopically a whole class of experimental systems as long as the repulsions do not predominate, but the reality of the associations modelled in this way can be problematic. A microscopic analysis shows that, as Onsager suggested, there are no good or bad criteria for defining chemical species in the case of weak interactions, as long as the problem is treated exactly. In fact, the two descriptions are equivalent. The only difference is that a chemical model describes microscopic states more precisely.

However, not all chemical models have the same potential. A relevant criterion for defining chemical species is to select the simplest model that minimises the excess free energy and therefore the deviations from ideality. However, this remains a delicate task, particularly for charged systems where electrostatic attraction is long-range. We have demonstrated here the general formulae for calculating the equilibrium constants of the mass action law from atomic models. This involves calculating an internal partition function averaged over the solvent configurations for the solutions. The result may depend on the standard state considered (choice of C°).

When put into action, this project will make it possible to characterise concentrated solutions using biased simulations. In most aqueous solutions, chemical speciation, both in free solutions and at interfaces, is mainly dictated, at least for single ions, by the formation of CIPs. At high concentrations, it is possible to predict a transition to macroscopic aggregation. Above a percolation threshold, the solution is mainly made up of a macroscopic species, sometimes called prenucleation cluster. The situation is then similar to that of micelles, but the aggregated solutes do not necessarily have a well-defined characteristic size.

An important point that has not been addressed is the study of transport phenomena. The ambiguity surrounding the definition of the species can be resolved more easily at the dynamic level, as the species have their own mobility.

Conflicts of interest

There is no conflicts to declare.



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