

The Activity Coefficient from a Solvation Thermodynamics Perspective

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Abstract: Activity is a central concept and quantity in thermodynamics because it unifies the description of several relevant functions and properties as well as it retains the simple logarithm form of the chemical potential. Because the activity is related to the concentration via the activity coefficient, the relationship between the chemical potential and the concentration is then established and the limit to ideal solution can be obtained by setting the activity coefficients to one. Thus, for real solutions, the activity coefficient embodies a wealth of information regarding the solute-solvent and solute-solute interactions and correlations as well as some other terms related to the choice of the standard state. The activity coefficient is then related to the solvation of a species (*e.g.*, solute) in a given environment (*e.g.*, solution). Thus, the proper definition of solvation and its use is relevant to interpret and quantify the activity coefficient. In this context, the solvation thermodynamics [1-3] formalism has been successful in defining solvation and removing several ambiguities in the conventional standard thermodynamic quantities.

The solvation thermodynamics is a molecular based description of the solvation concept and it provides a proper distinction from other processes such as liberation (momentum, volume sampling and indistinguishability). The main quantity in this formalism is the pseudo-chemical potential, $\mu_{i,\alpha}^*$, that represents the work to transfer the molecule *i* from a fixed position and orientation in the ideal gas phase to a fixed position and orientation within phase α , where for flexible molecules the conformation in the gas phase is maintained in phase α . Therefore, $\mu_{i,\alpha}^*$ quantifies the interactions between a reference molecule and its surroundings, which gives the proper meaning and expression for the solvation of this reference molecule.

We have shown that within the classical statistical mechanics, $\mu_{i,\alpha}^*$ can expressed exactly as, $\mu_{i,\alpha}^* = -k_{\rm B}T \ln\{q_i \langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha}\}$, where $k_{\rm B}$ is the Boltzmann constant, T the temperature, $\beta = (k_{\rm B}T)^{-1}$, q_i the internal partition function of i, and $E_{i,\alpha}$ is the binding energy defined as the difference between the potential energy of the system with imolecule inside, U_{N+i} , and the potential energy of the system without it, U_N , $E_{i,\alpha} :=$ $U_{N+i} - U_N$. It is noteworthy that this is exact and does not invoke the pairwise approximations in the definition and calculation of $E_{i,\alpha}$ present in previous derivations [1-4]. The activity coefficient, $\gamma_{i,\alpha}^{\rm ss}$, of i in phase α given the standard state ss is then expressed as $\gamma_{i,\alpha}^{\rm ss} := \exp[(\mu_{i,\alpha}^* - \mu_{i,ss}^*)/(RT)] = \langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha} / \langle e^{-\beta E_{i,ss}} \rangle_{N',ss}$. The ensemble averages $\langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha}$ and $\langle e^{-\beta E_{i,ss}} \rangle_{N',ss}$ involves different number of molecules



12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

(N, N'), because the environment of the standard state (ss) is distinct from that of the phase of interest (α), which can be evaluated from experimental solvation energy data $\Delta G_{i,\alpha}^*$, because $\langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha} = e^{-\beta \Delta G_{i,\alpha}^*}$, or from liquids theories or from molecular simulations (Monte Carlo, molecular dynamics).

In addition, the expression $\gamma_{i,\alpha}^{ss} = \langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha} / \langle e^{-\beta E_{i,ss}} \rangle_{N',ss}$ is the starting point to approximated approaches to calculate the activity coefficient, for instance, using the primitive model to describe electrolytic solutions or the small fluctuation approximation that allows the separation of the average binding energies $\langle E_{i,\alpha} \rangle_{N,\alpha}$ and $\langle E_{i,ss} \rangle_{N',ss}$ into a cavity and non-cavity contributions [5]. The cavity term can be described by analytical expressions based on scale particle theory [6], whereas the non-cavity contribution can be estimated from the interaction potential using the pairwise approximation or from implicit solvation models. Alternatively, this expression can be the starting point of a rigorous and feasible approach based on perturbation theory. For electrolytic solutions, the primitive model provides simple expressions for the activity coefficients of ions with the proper dependence with the concentration.

In addition to providing rigorous, general and alternative expressions and approaches, this formalism can give insightful and original interpretation for the activity coefficient. For instance, the difference in the average binding energies of species i within phases α and ss can be related to the activity coefficient, which provides a clear interpretation of how the distinct environments affect the activity of a given species.

This new formalism, interpretations and some applications will be explored during the presentation.

Key-words: binding energy, perturbation theory, solvation thermodynamics, activity. **Support:** This work has been supported by CAPES, CNPq, FACEPE, PRONEX, FINEP. **References:**

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