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Thermodynamics of Transfer of Atomic and Molecular Species into Binary Solvents

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Abstract—A method was suggested for separation of the Gibbs energy of transfer of atomic and molecular species from a solvent Solv1 into a binary solvent (Solv1 + Solv2) into the contribution from solvation of the reaction centers and that from nonspecific interactions, solvent reorganization, and cavity formation. The relationship for calculating the former contribution can be used for thermodynamically adequate comparative estimation of the stability of complex species in solution.

A solution containing an atomic or molecular species A in concentrations corresponding to pseudo-infinite dilution (<5 × 10^{-3} M) is ideal with respect to A (in the absence of self-association) both in solvent 1 (Solv1) and in a binary solvent (Solv1 + Solv2). Hence, by standardazing the chemical potential of A with respect to *P*, *T*, medium, and hypothetical 1 M solution with the properties of an infinitely dilute solution, we obtain for A

$$\mu_{C(\mathrm{A}),\,\mathrm{Solv1}} = \mu^{0}_{C(\mathrm{A}),\,\mathrm{Solv1}},$$
$$\mu_{C(\mathrm{A}),\,(\mathrm{Solv1+Solv2})} = \mu^{\otimes}_{C(\mathrm{A}),\,(\mathrm{Solv1+Solv2})}, \qquad (1)$$

where *C* denotes the molar concentration scale.

Since the standard media for Solv1 and (Solv1 + Solv2) are different (⊗ sign) and the other standardization parameters are identical, we obtain for the Gibbs energy of transfer of species A from Solv1 to (Solv1 + Solv2)

$$\Delta_{\mathrm{tr}}G^{0}_{C(\mathrm{A})\mathrm{Solv1}\to(\mathrm{Solv1+Solv2})} \neq \mu^{\otimes}_{C(\mathrm{A}),\,(\mathrm{Solv1+Solv2})} - \mu^{0}_{C(\mathrm{A}),\,\mathrm{Solv1}}. \qquad (2)$$

By standardazing $\mu^{\otimes}_{\mathrm{C(A),(Solv1+Solv2)}}$ with respect to Solv1, we obtain

$$\mu^{0}_{C(\mathrm{A}),\,(\mathrm{Solv1+Solv2})} = \mu^{0}_{C(\mathrm{A}),\,\mathrm{Solv1}} + RT\ln\Phi^{C}_{1} + RT\ln\Phi^{C}_{2}. \qquad (3)$$

According to Prigogine and Defay [1], the function Φ^{C}_{1} on the molar scale is defined as the fraction of species A, $\alpha_{(\mathrm{A}\cdot n\mathrm{Solv1})}$, that has not entered into interactions with the components of the binary medium (Solv1 + Solv2) different from the interactions in Solv1. The function Φ^{C}_{2} corresponds to specific (relative to Solv1) interactions of species A in the binary solvent. Passing to the unitary (mole fraction) scale (index *N*), i.e., to the standard state symmetrical with respect to all the components of the system, and taking into account the above definition of Φ^{C}_{1}, we obtain

$$\Delta_{\mathrm{tr}}G^{0}_{N(\mathrm{A}\cdot n\mathrm{Solv1})\mathrm{Solv1}\to(\mathrm{Solv1+Solv2})} = \mu^{0}_{N(\mathrm{A}),\,(\mathrm{Solv1+Solv2})} - \mu^{0}_{N(\mathrm{A}),\,\mathrm{Solv1}} = RT\ln\frac{x_{(\mathrm{A}\cdot n\mathrm{Solv1}),\,(\mathrm{Solv1+Solv2})}}{x_{(\mathrm{A}\cdot n\mathrm{Solv1})\mathrm{Solv1}}} + RT\ln\Phi^{N}_{2}$$
$$= RT\ln\alpha_{(\mathrm{A}\cdot n\mathrm{Solv1})} + RT\ln\frac{n^{0}_{\mathrm{Solv1}}}{a_{\mathrm{Solv1}} + a_{\mathrm{Solv2}}} + RT\ln\Phi^{N}_{2}, \qquad (4)$$

where $x_{(\mathrm{A}\cdot n\mathrm{Solv1}),\,\mathrm{Solv1}}$ and $x_{(\mathrm{A}\cdot n\mathrm{Solv1}),\,(\mathrm{Solv1+Solv2})}$ are the mole fractions of species A solvated in the short range with solvent 1 (A · *n*Solv1) in solvents Solv1 and (Solv1 + Solv2), n^{0}_{Solv1} is the number of moles of Solv1 in 1 l of this solvent, and a_{Solv1} and a_{Solv2} are the activities (M) of solvents 1 and 2 in the binary solvent. The use of activities of Solv1 and Solv2 instead of the numbers of their moles is due to the fact that the solution is ideal with respect to the solute A but generally nonideal with respect to the components of the binary solvent.

In view of data from [2, 3], the Gibbs energy of transfer of a species from one medium to another can be represented as a sum of contributions from short-range solvation (*in*), reorganization of the solvent around the particle (*r*) introduced into the cavity of the size matching the molecular size, formation of this cavity (*cav*), and difference between the dielectric permittivities of solvents 1 and 2 (*el*):

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$$\Delta_{\mathrm{tr}}G^{0}_{N} = \Delta_{\mathrm{tr}}G^{0}_{N,in} + \Delta_{\mathrm{tr}}G^{0}_{N,r} + \Delta_{\mathrm{tr}}G^{0}_{N,cav} + \Delta_{\mathrm{tr}}G^{0}_{N,el}. \qquad (5)$$

Thus, the function Φ^{N}_{2} is the unaccounted for contribution of the medium, which can be compared to the sum of the second, third, and fifth terms in Eq. (5), and the function Φ^{N}_{1} reflects changes occurring in the nearest surrounding of A. Then, the change in the Gibbs energy of transfer due to resolvation of A in the nearest surrounding can be reflected by

$$\Delta_{\mathrm{tr}}G^{0}_{N,in} = RT\ln\alpha(_{(\mathrm{A}\cdot n\mathrm{Solv1})} + RT\ln\frac{n^{0}_{\mathrm{Solv1}}}{a_{\mathrm{Solv1}} + a_{\mathrm{Solv2}}}. \qquad (6)$$

Thus, a new possibility arises of separating the total Gibbs energy of transfer of a species from one medium to another into contributions from the short- and long-range solvation on the quantitative level using known experimental methods.

Indeed, the quantity $\alpha_{(\mathrm{A}\cdot n\mathrm{Solv1})}$ can be determined from the law of mass action and material balance equation for reaction (7), which can be studied by one or another experimental method (see, e.g., [4, 5]).

$$[\mathrm{A}\cdot\mathrm{Solv1}_{n}] + m\mathrm{Solv2} \rightleftarrows [\mathrm{A}\cdot\mathrm{Solv1}_{(n-p)}\cdot m\mathrm{Solv2}] + p\mathrm{Solv1}. \qquad (7)$$

The quantities a_{Solv1} and a_{Solv2} can be determined from the vapor pressure [6]. The total Gibbs energy of transfer, $\Delta_{\mathrm{tr}}G^{0}_{N(\mathrm{A}\cdot n\mathrm{Solv1})\mathrm{Solv1}\to(\mathrm{Solv1}+\mathrm{Solv2})}$, is determined, e.g., by the solubility method [7] or some other procedure. The contribution of long-range solvation, which is poorly understood now, can be determined by subtracting the contribution of short-range solvation from $\Delta_{\mathrm{tr}}G^{0}_{N(\mathrm{A}\cdot n\mathrm{Solv1})\mathrm{Solv1}\to(\mathrm{Solv1}+\mathrm{Solv2})}$.

Finally, the developed concept allows the views on estimation of the relative stability of complex species in solution to be refined. The use of stability constants for this purpose has a number of limitations [8] and is often thermodynamically inadequate. It seems more appropriate to use for this purpose the Gibbs energy of transfer of a complex-forming ion from a medium containing no ligand L into a medium containing it. The work made by the system in such transfer is a thermodynamically adequate measure of the comparative stabilization of the complex-forming ion in one or another ligand-containing system. The calculation can be made by Eq. (8) if the interaction occurs in a binary solvent:

$$\Delta_{\mathrm{tr}}G^{0}_{N(\mathrm{A}\cdot n\mathrm{Solv1})\mathrm{Solv1}\to(\mathrm{Solv1}+\mathrm{Solv2})} = RT\ln\alpha_{(\mathrm{A}\cdot n\mathrm{Solv1})} + RT\ln\frac{n^{0}_{\mathrm{Solv1}}}{a_{\mathrm{Solv1}} + a_{\mathrm{Solv2}} + a_{\mathrm{L}}}. \qquad (8)$$

Generally, the denominator of the second term of Eq. (8) can include any number of components constituting the system.

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