

Reply to "Comment on 'Free Energy of Transfer of a Solute and Its Relation to the Partition Constant'"

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I offer the following comments in rebuttal to those of Graziano¹ regarding my paper.² The question under debate is what physical effects go into the free energy of transfer that is calculated according to eq 1

$$\Delta G_{i12}^{\circ} = -RT \ln K_{i12}^{\circ} \quad (1)$$

In my paper,² I have argued based on the evaluation of literature data that a discrepancy remains between the ΔG_{i12}° calculated from eq 1 and the intermolecular interactions of solute *i* in the considered phases 1 and 2. This discrepancy was very systematic (a constant value for a given system of phases 1 and 2) and appeared to support the theoretical analysis that has been put forward by Vitha and Carr before.³

Graziano criticized the additivity assumption that is implicit in my analysis. However, nonadditivity effects would not be able to explain the observed discrepancies and are unlikely to result in such systematic deviations. The effects of the end group (i.e., adding a CH₂ group instead of a CH₃ group) would even increase the observed discrepancy.

Graziano uses data for noble gases to prove the inadequacy of my approach. However, I do not understand how Graziano can apply the procedure that I used for alkanes to noble gases. Especially, I do not see any basis for Graziano's assumption (in his Figure 1) that He, Ne, Ar, and Kr correspond to a CH₂ group with respect to the free energy of transfer, while Xe and

Rn correspond to two CH₂ groups. This has nothing to do with the procedure that I used in my paper.

In addition to the data that I analyzed in ref 2, there is more evidence for such a discrepancy between ΔG_{i12}° calculated from K_{i12}° and the free energy of interaction of the solute in the respective phases: the linear solvation energy relationship (LSER) concept that has been developed by Abraham and co-workers^{4–10} is able to describe thousands of partition data in very diverse partition systems consistently and with high accuracy. In the LSER approach the logarithmic partition constant in molar concentrations, $\ln K_{i12}^{\circ}$, is expressed as a linear combination of free energy contributions that arise from the various intermolecular interactions between the solute and the solvents. These terms are the product of a solute property and the corresponding solvent properties, and they are derived empirically based on large experimental data sets. In addition to these interaction terms, all these equations do contain a constant contribution to $\ln K_{i12}^{\circ}$ (and thus to ΔG_{i12}°) that is significantly different from zero and that depends on the chosen solvent system.¹¹ Such a constant contribution should not exist if ΔG_{i12}° , calculated from eq 1, would reflect only intermolecular interactions.

References and Notes

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