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Effect of Solvent on Molecular Complex Formation. Correlation of Energy and Free Energy of Solution

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Recent reports from our laboratories have outlined a method for predicting the effect of solvation on molecular complex formation reactions.¹⁻³ The technique makes it possible to correlate the thermodynamic properties of the donor (D), acceptor (A) and complex (DA) involved in equilibria such as $D+A=DA$ by using a single parameter, α , defined by

$$\alpha = \frac{\frac{\Delta E_{DA}^{\circ}}{v \rightarrow s}}{\frac{\Delta E_D^{\circ}}{v \rightarrow s} + \frac{\Delta E_A^{\circ}}{v \rightarrow s}} = \frac{\frac{\Delta H_{DA}^{\circ}}{v \rightarrow s}}{\frac{\Delta H_D^{\circ}}{v \rightarrow s} + \frac{\Delta H_A^{\circ}}{v \rightarrow s}} \quad (1)$$

in which the ΔE° and ΔH° terms represent the changes in internal energy and enthalpy, respectively, for transferring one mole of a species (DA, D or A) from the ideal vapour phase (v) to the infinitely dilute solution in solvent (s). For several association reactions it has been shown that α varies only slightly with changes of solvent and that the analogous equation

$$\alpha = \frac{\frac{\Delta G_{DA}^{\circ}}{v \rightarrow s}}{\frac{\Delta G_D^{\circ}}{v \rightarrow s} + \frac{\Delta G_A^{\circ}}{v \rightarrow s}} \quad (2)$$

may be used to relate Gibbs free energy data; where standard states of 1 mole per liter, ideal dilute solution are used for each component in the vapour and in the condensed phase. Interaction energy parameters inferred from lattice treatments of non-electrolyte solutions⁴ have been successfully employed to predict in advance values of the useful parameter α .³

Consideration of the extensive collection of gas solubility data given by Hildebrand and Scott⁵ leads us to suggest that under fairly general conditions $\frac{\Delta E_i^{\circ}}{v \rightarrow s}$ and $\frac{\Delta G_i^{\circ}}{v \rightarrow s}$

may be linearly related for a variety of solutes (i) in a given non-polar or slightly polar solvent. Data for four typical non-polar solvents at 25°, taken from Appendix 3 of Ref. 5 and a recent report by Dymond,⁶ are plotted in Fig. 1 in the form $\frac{\Delta G_i^{\circ}}{v \rightarrow s}$ vs.

$\frac{\Delta E_i^{\circ}}{v \rightarrow s}$. The values have been calculated for

the required 1 mole/liter standard states by converting from pressure units and mole fractions to molarities and correcting for the thermal expansion of the solvent. Data for each solvent appear to be linearly related, with slopes of 0.63, 0.62, 0.64, and 0.51 for the solvents benzene, cyclohexane, CCl_4 , and perfluoroheptane, respectively.

That the plots in Fig. 1 are linear is not remarkable in view of the linearity of numerous plots of $\bar{S}_2 - S_2^g$ vs. $-R \ln x_2$ published by Hildebrand and Scott and their co-workers. However, use of the unit molarity standard states simplifies the correlation of thermodynamic data for associating species and facilitates the formulation of a method for predicting the effect of solvation on complex formation equilibria. If the molarity convention is employed, the equilibrium constant for distribution of a solute A between vapour and solvent, $K = [A(\text{solvent})]/[A(\text{vapour})]$, is dimensionless and approaches the value unity at the critical temperature of the solvent. Both at 0°K and at the critical temperature, $\frac{\Delta G_A^{\circ}}{v \rightarrow s} = \frac{\Delta E_A^{\circ}}{v \rightarrow s}$.

It might have been anticipated that each line should pass through the origin, corresponding to zero change in both energy and free energy. However, at $\frac{\Delta E_i^{\circ}}{v \rightarrow s} = 0$

the free energy change ranges from 400 to 500 cal/mole in the four solvents. Thus, the entropy of solution of a solute which dissolves with zero internal energy change

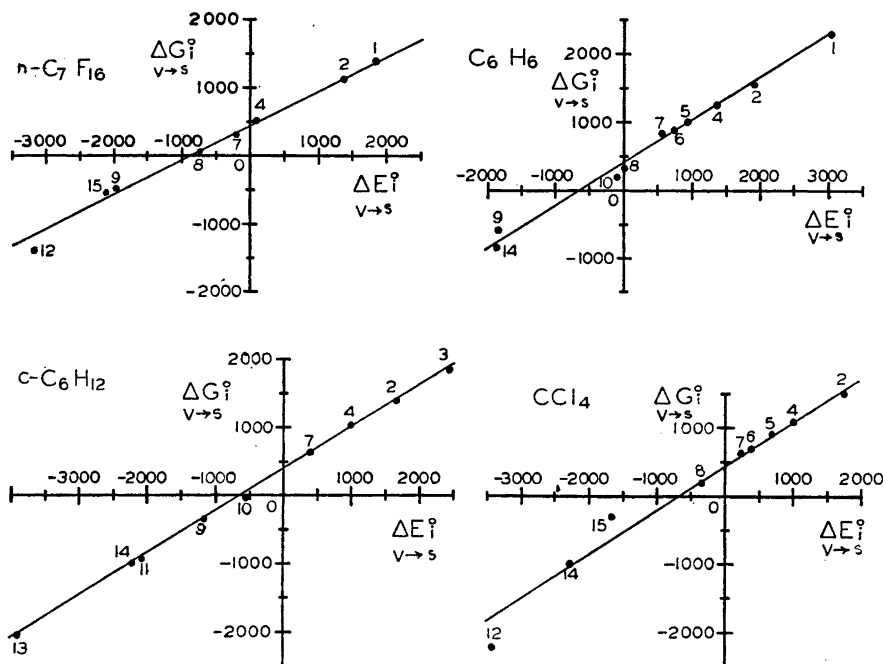


Fig. 1. Energy and free energy of solution of gases in cal/mole at 25°. 1, He; 2, H₂; 3, Ne; 4, N₂; 5, CO; 6, O₂; 7, Ar; 8, CH₄; 9 CO₂; 10, Kr; 11, Xe; 12, Cl₂; 13, c-C₃H₈; 14, C₂H₆; 15, SF₆. Standard states of solutes are 1 molar, ideal dilute solution for vapour and condensed phases.

is approximately $-R - (450/298)$ e.u. or $-1.75 R$. The negative entropy change probably owes primarily to a loss of solute translational and rotational degrees of freedom upon transfer to the condensed phase, independent of internal energy effects.

The empirical relation

$$\Delta G_{1\text{v}\rightarrow\text{s}}^{\circ} = \beta \Delta E_{1\text{v}\rightarrow\text{s}}^{\circ} + 0.75 RT \quad (3)$$

provides a good fit of data for each of the four solvents in terms of only a single parameter, β , which is characteristic of the solvent. Additional support for the validity of the relation is provided by its utility in correlating vapour pressure and heat of vapourization data for the pure solvents. From the vapour pressure and the molar volume of the solvent, $\Delta G_{1\text{v}\rightarrow\text{s}}^{\circ}$ may be calculated for the solvent for transfer between

the required 1 mole/liter standard states; $\Delta E_{1\text{v}\rightarrow\text{s}}^{\circ}$ may then be computed by using eqn. $\Delta G_{1\text{v}\rightarrow\text{s}}^{\circ}$

(3) with the value of β determined from Fig. 1. To obtain enthalpy values, a correction is made for the thermal expansion of the solvent and the pV term for the vapour. In this way, heats of vapourization have been predicted which differ from the experimental values by only 2.5% for benzene, 3.5% for cyclohexane, 2% for CCl₄, and 5% for perfluoroheptane. These results suggest that it may be feasible to calculate β solely from values of the heat of vapourization and vapour pressure of a solvent.

It the absence of strong specific solute-solvent interactions, linear relations of the type implied by eqn. (3) may be adequate to correlate thermodynamic data for individual donor, acceptor and complex molecules in a variety of solvents. A test of the equation may be made by considering the recently reported thermodynamic results for the formation of the charge-transfer complex between trimethylamine (D) and SO₂ (A).³ Values of $\Delta E_{1\text{v}\rightarrow\text{s}}^{\circ}$ and $\Delta G_{1\text{v}\rightarrow\text{s}}^{\circ}$ have

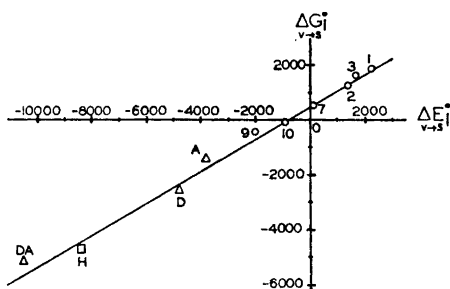


Fig. 2. Energy and free energy of solution in heptane at 25° (cal/mole). Non-polar solutes are coded as in Fig. 1; H, D, A, and DA represent heptane, $(\text{CH}_3)_3\text{N}$, SO_2 , and $(\text{CH}_3)_3\text{N}\cdot\text{SO}_2$, respectively. Standard states for all species are 1 mole/liter, ideal dilute solution for vapour and condensed phases.

been given for the individual species (D, A, and DA) for transfer from the vapour phase to dilute solution in heptane at 25°. These values are displayed in Fig. 2, along with data for other solutes (coded as in Fig. 1) and the pure solvent. The points representing data for the species involved in the charge transfer reaction lie nearly on the line defined by the non-polar solute species. The value of δ determined from the slope of the straight line is 0.59.

The utility of the linear correlation may be more clearly illustrated by employing the results in Fig. 2 to predict ΔE° for the complex formation reaction ($\text{D} + \text{A} = \text{DA}$) in heptane from the reported ΔE° for the reaction in the vapour phase (-9.1 kcal.). Employing eqn. (3) and the appropriate thermodynamic cycle,

$$\begin{aligned} \Delta E^\circ_{\text{heptane (vapour)}} &= \Delta E^\circ + \frac{1}{\beta} \left[(\Delta G^\circ_{\text{DA}} - 0.75 RT)_{\text{v} \rightarrow \text{s}} - (\Delta G^\circ_{\text{A}} - 0.75 RT)_{\text{v} \rightarrow \text{s}} - (\Delta G^\circ_{\text{D}} - 0.75 RT)_{\text{v} \rightarrow \text{s}} \right] \\ &= -9.1 + \frac{1}{0.59} \left[-5.15 - 0.45 + 1.40 + 0.45 + 2.57 + 0.45 \right] \\ &= -10.4 \text{ kcal.} \end{aligned}$$

which agrees reasonably well with the measured value (-11.1 kcal.).

The energy-free energy correlation proposed here should be tested by considering solvation data for numerous complex-formation reactions; unfortunately, adequate results are available for very few associating systems. We are currently attempting to obtain accurate solvation data

for several hydrogen-bonding and charge-transfer reactions. For systems in which the dipole moment of the complex (DA) is not considerably greater than the sum of the dipole moments of D and A, it appears to be justifiable to calculate $\Delta E^\circ_{\text{D}}$, $\Delta E^\circ_{\text{A}}$, and $\Delta E^\circ_{\text{DA}}$ (and hence α) from specific group interaction energies derived from a lattice treatment of solutions.³ By utilizing the calculated values of $\Delta E^\circ_{\text{D}}$ and the value of β characteristic of the given solvent, it is possible to predict the effect of solvation on both ΔE° and ΔG° for the complex-formation reaction, even in the absence of solvation data for D, A, or DA. In addition, by a two step process involving the vapour as an intermediate state, it is possible to predict the changes in ΔE° and ΔG° for the association reaction as the medium is changed from one solvent to another.

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