

A Critical Examination of the Limiting Activity Coefficients of Normal Alkanes in Common Organic Liquids

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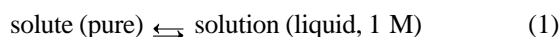
The activity coefficients of alkanes used to be the data of importance in many fields of chemistry, including chromatography,¹⁻⁵ physical organic chemistry^{6,7} and chemical engineering.⁸⁻¹⁰ Alkanes are the least complex probe solutes because the only possible attractive forces between an alkane and the solvent are dispersive interactions.

In the previous papers, we critically examined the effect of solute structure¹¹ and solvent structure¹² on the logarithmic gas/liquid partition coefficients.

In this study, the logarithmic activity coefficients of normal alkanes have been critically discussed. The same data set of the previous papers have been used.

Theory

The activity coefficient of a solute in a liquid solvent is related to the Gibbs free energy of solute transfer from its pure state into the liquid as follows¹³:



$$\Delta G^\circ = RT \ln \gamma \quad (2)$$

The solute activity coefficient can be experimentally determined by measuring the gas/liquid partition coefficient of the solute.¹¹

The following relationship is well known for a homologous series of solutes.

$$\Delta G^\circ = \Delta G^\circ_a + n \Delta G^\circ_b \quad (3)$$

where ΔG°_a is the head group contribution to the total free energy of transfer, n , the number of CH_2 or CH_3 groups, and ΔG°_b , the CH_2 (or CH_3) group contribution.

Equation 3 can be easily converted to Equation 4.

$$\ln \gamma = a + n b \quad (4)$$

where $a = \Delta G^\circ_a / (RT)$, and $b = \Delta G^\circ_b / (RT)$.

The methylene group (CH_2) contribution to the free energy of solute transfer from the pure solute to the solvent can be divided into two components: the cavity formation free energy term ($\Delta G^\circ_{\text{CH}_2, \text{cav}}$) and the interaction free energy term ($\Delta G^\circ_{\text{CH}_2, \text{int}}$).

$$\Delta G^\circ_{\text{CH}_2} = RT b = \Delta G^\circ_{\text{CH}_2, \text{cav}} + \Delta G^\circ_{\text{CH}_2, \text{int}} \quad (5)$$

The cavity formation term is the cavity formation energy in the solvent minus the cavity formation energy in the pure solute liquid. The cavity formation energy is required to make a cavity for the CH_2 unit in the solvent. The cavity

formation term will be near 0 when the solvent is nonpolar, and will get larger as the solvent polarity gets higher. The interaction free energy term is the interaction of a CH_2 unit with the solvent minus the interaction of a CH_2 unit with the pure solute liquid. The interaction free energy term is expected to be 0 or slightly negative since the dispersive energies are predominant and similar in both phases. In the case of solute transfer to a polar solvent, the interaction free energy in the solvent will be slightly more negative than the interaction free energy in the pure solute since there is an additional weak interaction: the polar solvent dipole-solute induced dipole interaction. In summary, the interaction free energy term will be much less significant than the cavity formation free energy term, and the overall free energy of transfer of the CH_2 unit will be either near 0 or positive and will increase with the solvent polarity. In other words, the slope in the plot of $\ln \gamma$ vs. solute carbon number will be positive and will get higher as the solvent polarity gets more polar.

Since the cavity formation energy is approximated as the product of solute size with the square of solvent solubility parameter (δ^2),^{14,15} and the cavity formation energy of a CH_2 unit in a pure nonpolar solute (alkane) is virtually invariant, $\Delta G^\circ_{\text{CH}_2}$ is expected to correlated linearly with δ^2 . The solubility parameter (δ) is defined as the square root of the solvent heat of vaporization (cal) per unit solvent volume (mL).

$$\Delta G^\circ_{\text{CH}_2} = k_1 + k_2 \delta^2 \quad (6)$$

Results and Discussion

The slopes in the plots of $\ln \gamma$ vs. solute carbon number are close to 0 for nonpolar solvents and get larger with increasing solvent polarity as discussed in the theory section. Such plots are shown in Figure 1 for some selected solvents. Not only the slope but also the absolute value of $\ln \gamma$ increase with increasing solvent polarity as shown in Figure 1. We also note that the $\ln \gamma$ values of n -alkanes in a very nonpolar solvent such as hexane are close to 0.

We calculated the methylene group transfer free energy for each solvent from its slope in the plot of $\ln \gamma$ vs. solute carbon number and plotted it against the solvent cohesive energy density (square of solvent solubility parameter, δ^2) in Figure 2 to examine if equation 6 is valid. The correlation is not good ($r = 0.81$, $n = 45$) although a coarse correlation is observed. The cavity formation seems to be a too complicated process to be described by a single major parameter.

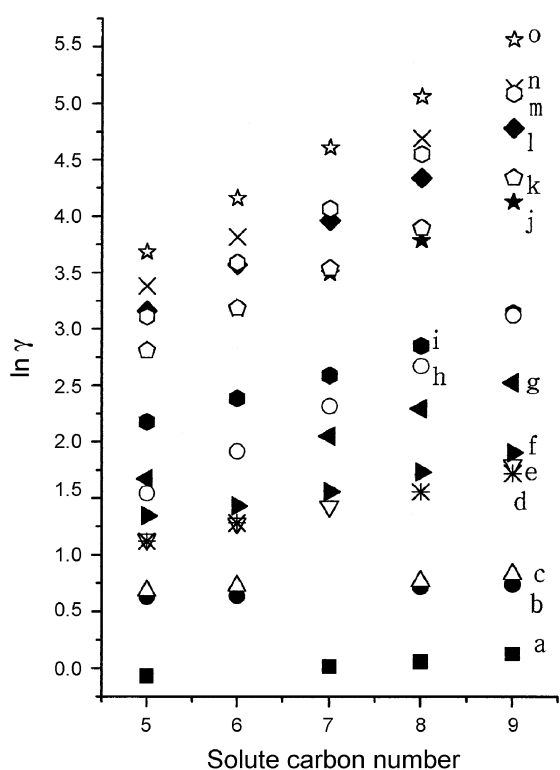


Figure 1. The plots of $\ln \gamma$ of alkane solutes vs. solute carbon number for some selected solvents. a; hexane, b; tetrahydrofuran, c; benzene, d; ethylacetate, e; dichlorobenzene, f; hexamethylphosphotriamide, g; acetone, h; perfluorooctane, i; dimethylacetamide, j; methanol, k; acetonitrile, l; methylformamide, m; trifluoroethanol, n; nitromethane, o; dimethylsulfoxide.

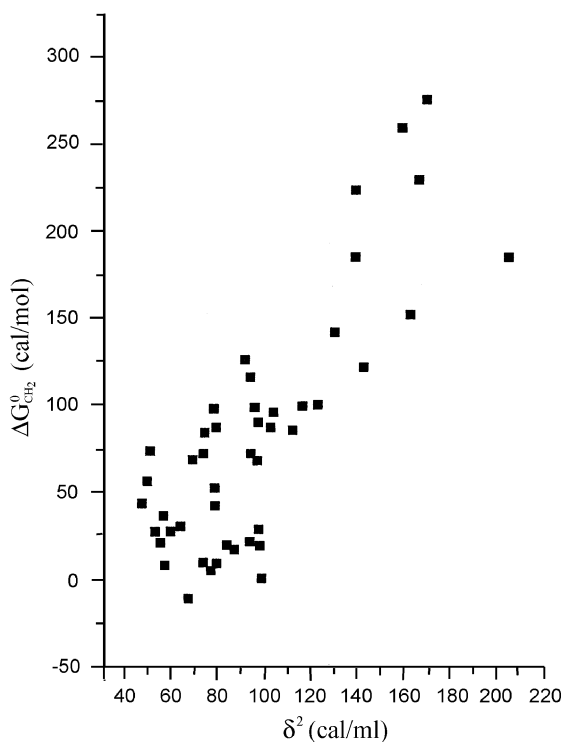


Figure 2. The correlation of the free energy of transfer of the solute CH_2 unit with the solvent cohesive energy density.

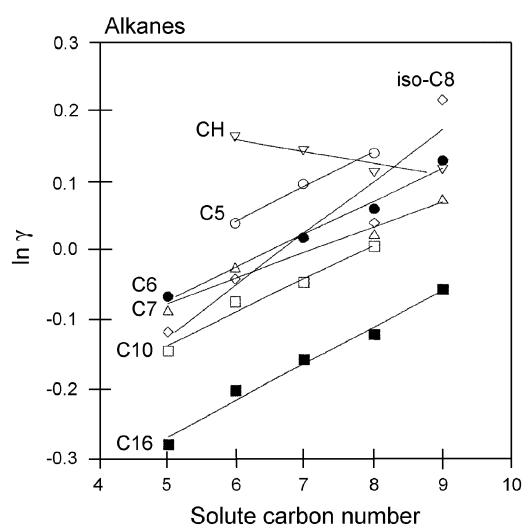


Figure 3. The plots of $\ln \gamma$ of alkane solutes vs. solute carbon number for alkane solvents. C5; pentane, C6; hexane, C7; heptane, iso-C8; iso-octane, CH; cyclohexane, C10; decane, C16; hexadecane.

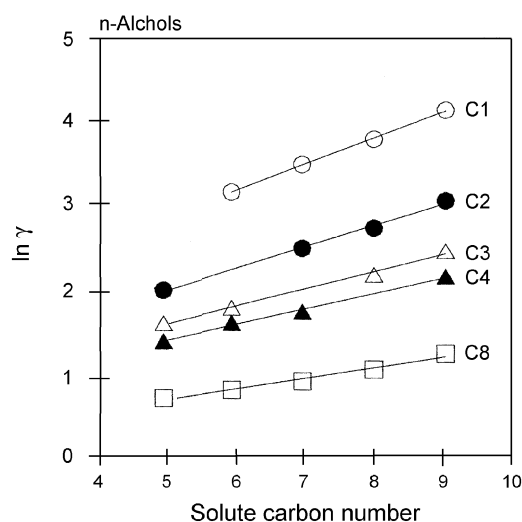


Figure 4. The plots of $\ln \gamma$ of alkane solutes vs. solute carbon number for some alcohol solvents. C1; methanol, C2; ethanol, C3; n-propanol, C4; n-butanol, C8; n-octanol.

We comparatively examined variations of $\ln \gamma$ with respect to solute carbon number for three solvent groups: alkanes, alcohols, and nitriles. Such plots are given in Figures 3, 4, and 5. It is well illustrated in Figures 4 and 5 that the $\ln \gamma$ values and the slopes of the lower members (lower carbon number, more polar) of the homologous series of solvents are higher than those of the higher members (higher carbon number, less polar) for alcohols and nitriles as was expected on the basis of the above theoretical background.

There are some peculiar points in Figure 3. The $\ln \gamma$ values and the slopes in the plots of $\ln \gamma$ vs. solute carbon number for alkane solvents are close to 0 as was expected on the basis of the theoretical background. However, even negative $\ln \gamma$ values are observed. We found that negative $\ln \gamma$ were found only in alkane solvents when the size of alkane solvent is larger than the size of alkane solute. Thus $\ln \gamma$ values in decane and hexadecane are all negative since

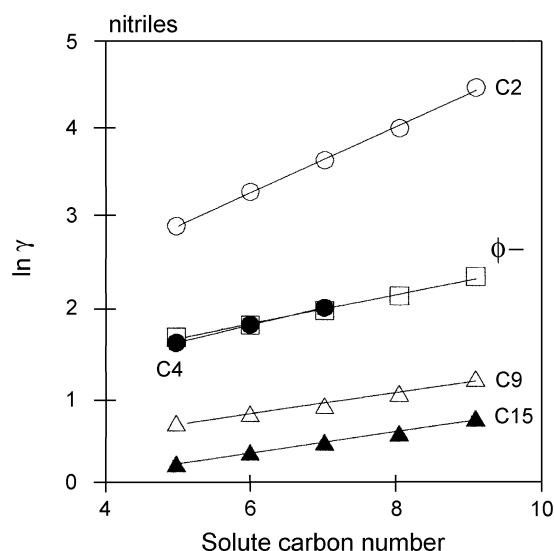


Figure 5. The plots of $\ln \gamma$ of alkane solutes vs. solute carbon number for some selected solvents. C2; acetonitrile, C4; butyronitrile, Φ^- ; benzonitrile, C9; nonanenitrile, C15; pentadecanenitrile.

solutes are pentane, hexane, heptane, octane, and nonane. The negative $\ln \gamma$ means that an alkane solute prefers to transfer from its pure state to a bigger alkane solvent (for example, hexadecane). The absolute magnitude of $\ln \gamma$ gets larger when the size difference between the solute and the solvent gets larger. The negative value in $\ln \gamma$ corresponds to a smaller cavity formation energy in the solvent for the solute than that in the pure solute or to a stronger solute-solvent interaction (more negative interaction energy) than the solute-solute interaction in pure solute. It is unlikely that the cavity formation energy of the solute in the solvent is smaller than that in the pure solute since the cohesive energy density of solvent (larger alkane) is larger than that of solute (smaller alkane) even though the difference is slight, but it is reasonable that the interaction of a solute molecule with large solvent molecules (large dispersion forces) is stronger than the interaction of the solute molecule with small solute molecules. In a more polar solvent than alkanes, the cavity formation energy of the solute in the solvent is larger than that in the pure solute and the interaction of the solute with solvent molecules is stronger than the interaction of the solute with solute molecules, but the cavity formation effect is dominant and negative $\ln \gamma$ values are not observed except for large alkane solvents.

Another unique point of Figure 3 is the plot of cyclohexane solvent. Its slope is negative. Cyclohexane is the only solvent that gives a negative slope in the plot of $\ln \gamma$ vs. solute carbon number in the whole solvent set, and it is the only cyclic alkane in the solvent set. The meaning of negative slope is that the increase of solute size is favored when the solute is transferred from its pure state to cyclohexane. In other words, a decrease of difference in cavity formation energy for the solute between pure solute and cyclohexane or a stronger solute-cyclohexane interaction relative to the solute-solute interaction is expected with a larger alkane solute.

The solubility parameter of cyclohexane is 8.196, and that of n-hexane, 7.272. Thus a ring structure of molecule causes a stronger dispersive interaction than a chain structure. Actually the solubility parameter of cyclohexane is larger than that of any solute used (pentane to nonane) in this study. Thus the cavity formation energy for the solute in cyclohexane is always larger than that in the pure solute phase. Therefore it is likely that the difference in cavity formation energy for the solute between pure solute and cyclohexane increases with the increased solute size since the cavity formation energy increases with the solute size. The cavity formation effect (expected increase of difference in cavity formation energy with increased solute size) is against the observed negative slope in the plot of $\ln \gamma$ vs. solute carbon number. Thus we have to conclude that the negative slope of cyclohexane in the plot of $\ln \gamma$ vs. solute carbon number is owing to a stronger solute-cyclohexane interaction relative to the solute-solute interaction for a larger solute. Such effect should be strong enough to override the opposing cavity formation effect (expected increase of difference in cavity formation energy for the solute between pure solute and cyclohexane with increased solute size, contributing to a positive slope in the plot of $\ln \gamma$ vs. solute carbon number as explained above). We guess the flat structure of cyclohexane explains this phenomenon. The dispersive interaction between the solute and the planar solvent is inefficient if the solute size is too small since it is difficult for the solute to be surrounded by as many planar solvent molecules as possible. Thus the efficiency of dispersive solute-solvent interaction gets higher as the solute size increases and this contributes to a negative slope in $\ln \gamma$ vs. solute carbon number.

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