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Hydrophobic hydration from solubilities of aliphatic hydrocarbons in water

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ABSTRACT

The internal standard transfer Gibbs energy, $\Delta G^0_{t,int}$ is computed by subtracting corresponding standard transfer Gibbs energy, ΔG^0_t of solute hydrocarbons due to cavity and different interactions from the total ΔG^0_t value as obtained from the available experimental solubility of them in water (w). For alkanes other possible interaction effects being negligibly small, $\Delta G^0_{t,int}$ is a direct measure of hydrophobic hydration. The various $\Delta G^0_{t,int}$ values of >CH_2 group evaluated from the difference of $\Delta G^0_{t,int}$ values of two successive members of homologous alkanes, is found to be highly precise in respect to their average, 3.95 kJ mol^{-1}, indicating additive nature of the parameter. $\Delta G^0_{t,int}$ values of different fractions are found to follow the order: –CH_3 > –CH_2– ≫ CH– ≫ C<. Aliphatic hydrocarbons possessing the same number of C atom follows the sequence: alkane > alkene > alkyne, according to their reverse order of polarizability and acidity in water.

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1. Introduction

The hydrophobic effect is perhaps the single most important phenomenon in the entropy driven creation of various 'self-aggregated systems' like micelles, vesicles, bilayer membranes, association of hydrocarbons (HC) and amphiphiles with proteins, etc. It also stands for the organization of the constituent molecules of living matter into complex structural entities such as cell membranes and organelles. In spite of its influences in all these systems and its long day's recognition of having multitudinous effects, the estimation of Gibbs energy of the involved hydrophobic interaction (HI) and particularly that of the closely related hydrophobic hydration (H$_b$H) are still not unequivocally made. Moreover, the direct experimental determination of these are also not directly viable [1,2]. On the other hand it is well known [3–9] that hydrophobic hydration or 'the hydration of the second kind' arises due to the strong attraction or affinity of water molecules for one another. The hydrophobic, amphiphalic or amphiphilic solutes with a polar sites, not being strongly attracted by water, pushes them closer and thus easily induce more water molecules around them with the formation of a cage in a way similar to clathrate hydrates. This results in a significant increase in Gibbs energy and decrease in entropy [10]. Thus the phenomenon is significantly guided by the water-water interaction associated with the related structural and entropy effect [10]. But the relative contributions of the involved interactions of different parts of

the molecule, say –CH_3, –CH_2–, >CH–, >C<, –CH=CH_2 etc. are still not clear. Thus if anyone can subtract the transfer Gibbs energy part due to cavity and all possible interactional effects or at least the major contributory parts of it from the total experimental Gibbs energy of solution, one can get the rest of the entropy-contributed transfer Gibbs energy effect as designated by $\Delta G^0_{t,int}$ and thus can understand and elucidate the possible structural change associated with the hydrophobic effect. With this aim in mind, the phenomenon here chosen is one that provides plausibly the simplest manifestation of the hydrophobic effect — the meager solubility of hydrocarbons in water. In fact, in most of the previous studies [11–19], as found from the literature, H$_b$H has been estimated and understood in association with the dispersion interaction, which is somewhat akin to hydrophobic interaction (HI) and acted as a reversal of H$_b$H. From statistical mechanical consideration, Arieh Ben-Naim [20,21] expressed his doubt regarding the relative importance of the hydrophobic interaction because such interaction arises not due to unique peculiarities of liquid water but to strong solvent–solvent interaction. In some old studies [15,16,22–24] efforts made to understand HI and H$_b$H from a set of data where effect of all three different types of involved interactions namely, solute–solute, solute–solvent and solvent–solvent interactions are intermixed. Moreover in many previous studies, H$_b$H were understood without the consideration of the Gibbs energy change associated with the formation and collapsing of an appropriate cavity in water and hydrocarbon (HC) liquid respectively i.e., the transfer Gibbs energy (ΔG^0_t) due to the so-called cavity effect, $\Delta G^0_{t, cav}$. In fact the application of the scaled particle theory, which was originally devised for calculating the reversible

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work required for a hypothetical hard sphere solute to form a cavity in a hypothetical hard sphere liquid, into the domain of real solute and real fluid, has developed latter [18,19]. In some studies [3,25] H_bH is obtained by eliminating all the attractive interactional effects like dipole–dipole (dd), dipole-induced dipole (ind), dispersion (dis) from the experimental energetics excluding cavity effect. However, this result seems to fail to point out the special property of hydrophobic solute i.e., H_bH, since cavity effect would be present in all types of solute–solvent interactions, including that of hydrophilic solute. So it is thought that an effort to understand HI and particularly H_bH directly from the experimental values of solubility of hydrophobic solute in water, without considering the above mentioned effects, may lead to erroneous conclusions and increase confusion, both of which still persist in spite of the importance and long day's recognition of the phenomenon.

Moreover the initial transfer Gibbs energy of $-CH_2-$ group, which may produce hydrophobic hydration, is not found to be a unique quantity since it depends on other molecular parts with which it is attached, in aqueous DMF solvent system as evident from our previous study [26]. This is seemingly because of the different interactions of groups like $-CH_3$, $-CH_2-$, $>CH-$ with different functional groups of the probe molecules such as carboxylate and amino groups of some lower members of homologous series of α-amino acids used in many studies [26]. It seems that the proper value of hydrophobic hydration could be obtained under the condition where $-CH_2-$ and other groups do not interact with the functional groups of the molecules. In this regard pure saturated hydrocarbon can play a significant role as a probe in understanding hydrophobic hydration, since it has no functional group. In absence of literature values of solubility of pure hydrocarbons in DMF–water solvent system, computation of hydrophobic hydration of $-CH_2-$ group is executed by using the literature values of meager solubility of hydrocarbon in water [27] in this study.

Thus in the present study, transfer Gibbs energy contributions due to cavity formation ($\Delta G^0_{t,cav}$), dispersion interaction ($\Delta G^0_{t,dis}$), dipole–dipole interaction ($\Delta G^0_{t,dd}$), dipole–induced dipole interaction ($\Delta G^0_{t,ind}$) have been computed for transfer of one mole of different hydrocarbon (HC)s from the respective infinitely large HC liquid system to an infinitely large pure water system. The summation of all such ΔG^0_t gives rise theoretical Gibbs energy of transfer which on subtraction from the total/experimental ΔG^0_t values, evolves the internal Gibbs energy of transfer ($\Delta G^0_{t,int}$), which in turn provides H_bH.

Thus the total or experimental ($\Delta G^0_{t,expt}$) and theoretical ($\Delta G^0_{t,theo}$) Gibbs energy of transfer of HC from HC liquid to water (w) are given by Eqs. (1) and (2):

$$_{HC}^{w}\Delta G^0_{t,expt} = {}_{HC}^{w}\Delta G^0_{t,theo} + {}_{HC}^{w}\Delta G^0_{t,int} \qquad (1)$$

and

$$_{HC}^{w}\Delta G^0_{t,theo} = {}_{HC}^{w}\Delta G^0_{t,cav} + RT \ln (V_{HC}/V_w) + {}_{HC}^{w}\Delta G^0_{t,dis} + {}_{HC}^{w}\Delta G^0_{t,dd} + {}_{HC}^{w}\Delta G^0_{t,ind} \qquad (2)$$

where suffix t indicates the transfer process from standard state of HC to that of water, V_i the molar volume of the ith liquid and all other quantities are as usual [11–14]. Here all the terms of RHS of Eq. (2) can be theoretically calculated and $_{HC}^{w}\Delta G^0_{t,int}$ can be obtained from Eq. (1). It seems to be constituted by the transfer Gibbs energy due to the structural or entropy change of the solvent (H_bH) as well as ΔG^0_t for the existing interactions in the system which are not computed. One such example is the solvent (w)–solvent (w) interaction, on the said transfer of HC.

The total Gibbs energy of transfer $_{HC}^{w}\Delta G^0_t$ in mole fraction scale, can be had from the experimental solubility data [17] by using the relation

$$_{HC}^{w}\Delta G^0_{t,expt} = {}_{HC}^{w}\Delta G^0_t = -RT \ln X. \qquad (3)$$

Table 1.1
Molar volume ($V \times 10^{-6}$ m^3), diameter ($\sigma \times 10^{-10}$ m) and volume polarizability ($\alpha \times 10^{-30}$ m^3) of different alkanes, alkenes and alkynes.

No. of C atoms	Alkanes			Alkenes			Alkynes		
	V	σ	α	V	σ	α	V	σ	α
C_5	115.2	5.78	10.01	109.5	5.67	9.85	98.7	5.45	9.17
C_6	130.7	6.07	11.85	125.0	5.97	9.88	114.8	5.77	11.00
C_7	146.5	6.34	13.69	140.8	6.24	11.71	131.2	6.08	12.85
C_8	162.6	6.59	15.53	157.0	6.50	15.58	147.7	6.35	14.68
C_9	178.7	6.83	17.37	172.9	6.74	17.12	164.1	6.61	16.52
C_{10}	194.9	7.05	19.14	189.4	6.98	19.04	180.6	6.85	18.35
C_{11}	211.2	7.27	22.04	205.7	7.20	20.88	197.0	7.08	20.19

Branch-chain alkanes	V	σ	α
2-Methylpentane	131.9	6.09	11.87
3-Methylpentane	129.7	6.05	11.80
2,4-Dimethylpentane	148.9	6.37	13.72
2,2-Dimethylbutane	132.7	6.10	11.87
2,2,4-Trimethylpentane	165.1	6.63	15.56
2,2,5-Trimethylhexane	181.3	6.86	17.41

Thus the difference between the experimental and theoretical values of ΔG^0_t will provide $_{HC}^{w}\Delta G^0_{t,int}$ which seems to contain ΔG^0_t for structural (H_bH) effect along with that for other possible unaccounted interactions existing in the system.

In the case of saturated aliphatic hydrocarbons, all possible types of solute–solute and solute–solvent interactions can be counted by considering the terms expressed in Eq. (2). Thus $\Delta G^0_{t,int}$ is purely a composite measure of transfer Gibbs energy associated with the entropy change of solute and solvent i.e. (H_bH) or ($\Delta G^0_{t,st}$) as well as that for the solvent (w)–solvent (w) interaction ($\Delta G^0_{t,w-w}$) on such transfer of HC i.e.,

$$\Delta G^0_{t,int} = \Delta G^0_{t,st} + \Delta G^0_{t,w-w}. \qquad (4)$$

Moreover, since the successive members of any homologous series, always possess a difference of $-CH_2-$ group constitutively, it would be interesting to see whether a fixed value of $\Delta G^0_{t,int}$ can be obtained from the difference of group of $\Delta G^0_{t,int}$ values of any two successive members of the same homologous series i.e., to check whether $\Delta G^0_{t,int}$ or H_bH is an additive property of the different fractions of a molecule.

With this view in mind, we have presented here $\Delta G^0_{t,int}$ for all the alkanes alkenes and alkynes possessing C atoms from 5 to 11.

2. Method of calculation

The transfer Gibbs energy of hydrocarbon (HC) molecule from HC liquid to an infinitely dilute aqueous solution of HC, as represented by $_{HC}^{w}\Delta G^0_t$ (HC), may essentially be thought to consist of two steps: (1) transfer of HC from HC liquid to vacuum — the corresponding transfer Gibbs energy change is $_{HC}^{v}\Delta G^0_t$(HC) and then (2) transfer of HC from vacuum to an infinitely dilute solution of HC in water—the corresponding transfer Gibbs energy change is $_{v}^{w}\Delta G^0_t$ (HC).

Thus

$$_{HC}^{w}\Delta G^0_{t,theo}(HC) = {}_{v}^{w}\Delta G^0_t(HC) + {}_{HC}^{v}\Delta G^0_t(HC). \qquad (5)$$

Table 1.2
Dipole moment (μ) and average dipole moment of different alkanes, alkenes and alkynes.

Hydrocarbon	μ (Debye)	Avg. μ (Debye)
Alkanes: propane	0.09	0.09
Alkenes: propene	0.36	
Butene	0.34	0.35
Alkynes: pentyne	0.81	
Hexyne	0.83	0.82