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STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

The RISM Method for Estimating the Thermodynamic Characteristics of Hydration of Saturated Hydrocarbon Molecules

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Abstract—The thermodynamic characteristics of hydration of various saturated hydrocarbon molecules were calculated. A system of empirical parameters substantially improving agreement between calculated and experimental values was obtained.

In recent years, the RISM (Reference Interaction Site Model) method has been extensively used for estimating the thermodynamic characteristics of hydration along with various empirical, molecular dynamics, and Monte Carlo methods. It has been shown in [1] that the RISM method gives qualitatively correct estimates of the Gibbs energy ($\Delta G°$) of hydration of various conformers of hydrocarbon molecules, in which molecular fragments are differently arranged with respect to each other. This means that the method correctly reproduces the dependence of $\Delta G°$ on the mutual arrangement of fragments spaced apart along molecular chains. The empirical methods are incapable of doing this, but they fairly accurately reproduce contributions corresponding to short-range interfragment interactions, and are therefore complementary to the RISM method. It is natural to suggest that the introduction of certain empirical corrections to the $\Delta G°$ values obtained by the RISM method would improve their agreement with experiments. In this work, we describe one of possible correlation equations for determining the $\Delta G°$ values of saturated hydrocarbons.

The principal points of the theory can be found in [2, 3]. An algorithm for solving equations and a variant of its implementation are described in [4]. These programs were used in this work. All calculations were performed for 25°C and water density $\rho = 0.997$ g/cm^3 with the use of various "closure conditions." Generally, closure conditions are equations including a single parameter s [5]. The $s = 1$ value corresponds to the hyperchain closure, and $s = 2$, to the Martynov–Sarkisov closure [6]. Generally, s can be treated as an adjustment parameter the selection of which allows experimental data on some compound to be reproduced. For instance, at $s = 1.79$, we obtain the $\Delta G°$ value for methane. At present, there is no clear idea of the quality of various approximations (closure conditions), and, in the tables, we give results obtained for several closure equations. Their comparison with experiment allows us to give preference to one or another approximation in each particular case.

The approach developed in [1, 4] was used to calculate the thermodynamic characteristics of hydration of several saturated hydrocarbon molecules, some of which are included in Table 1. The calculations give fairly close agreement with the experimental ΔE values, and much worse agreement for $\Delta G°$. Some of the experimental and calculated $\Delta G°$ values differ not only in magnitude but also in sign. This means that the RISM method in the described variant can hardly be considered a promising approach to calculating $\Delta G°$.

On the other hand, the RISM method often correctly reproduces trends in changes of the thermodynamic characteristics of hydration. For instance, for linear hydrocarbon molecules except ethane and propane, these values linearly increase with the length of the chain, *trans* configurations of molecules have larger $\Delta G°$ values than more compact configurations, which agrees with the data of Monte Carlo calculations and is in conformity with the generally accepted views. This leads us to conclude that the RISM method qualitatively correctly reproduces the dependence on the mutual arrangement of fragments spatially separated along the chain, which is beyond reach of all empirical schemes for calculating the thermodynamic characteristics of hydration. Indeed, any property of a molecule can be written as [7, 8]

$$P = \sum_i P_{ii} + \sum_{i,j} P_{ij}, \qquad (1)$$

where P_{ii} is the one-fragment contribution corresponding to the ith fragment (atom), and P_{ij} is the two-fragment contribution corresponding to interaction between the ith and jth fragments. The P_{ij} values usually decrease as the distance between the fragments increases, and the major contributions are therefore

Table 1. Thermodynamic characteristics of some hydrocarbon molecules

Molecule	$\Delta G°$, kJ/mol				$-\Delta E$, kJ/mol			
	expt. [9]	$s = 1$	$s = 2$	$s = 1.79$	MC [10]	$s = 1$	$s = 2$	$s = 1.79$
CH_4	8.40	36.32	5.02	8.36	12.08	7.36	10.91	10.49
$CH_3–CH_3$	7.69	51.37	6.65	11.83	20.06	14.67	18.77	18.31
$CH_2–CH_2–CH_3$	8.19	68.13	7.94	14.92	27.59	20.61	25.62	25.08
$CH_3–(CH_2)_2–CH_3$ *t*	8.74	88.11	9.82	18.89		25.25	31.64	30.97
$CH_3–(CH_2)_2–CH_3$ *g*		82.89	9.07	17.72		21.74	26.79	26.25
$CH_3–(CH_2)_3–CH_3$ *tt*	9.78	106.84	12.67	23.62		30.39	37.83	37.08
$CH_3–(CH_2)_3–CH_3$ *tg*		104.21	11.08	21.90		30.85	38.00	37.24
$CH_3–(CH_2)_3–CH_3$ *gg*		98.86	9.28	19.67		32.52	38.87	38.25
$CH_3–(CH_2)_3–CH_3$ *gg'*		94.09	9.32	19.35		33.31	39.29	38.67
$CH_3–(CH_2)_4–CH_3$ *ttt*	10.45	124.90	15.05	27.88		35.82	44.14	43.26
$CH_3–(CH_2)_4–CH_3$ *ttt*		123.52	13.96	26.67		35.70	43.93	43.10
$CH_3–(CH_2)_4–CH_3$ *tgt*		123.85	13.59	26.38		35.66	43.93	43.14
$CH_3–(CH_2)_4–CH_3$ *tgg*		120.38	11.83	24.41		36.32	44.10	43.37
$CH_3–(CH_2)_5–CH_3$ *tttt*	10.99	143.84	17.18	31.98		40.88	50.29	49.37
$CH_3–(CH_2)_5–CH_3$ *tttg*		140.95	16.47	31.02		41.42	50.33	49.49
$CH_3–(CH_2)_5–CH_3$ *ttgt*		143.17	16.26	30.97		40.50	49.78	48.86
$CH_3–(CH_2)_5–CH_3$ *tggt*		141.83	14.50	29.18		40.04	49.28	48.40
$C(CH_3)_4$	10.49	108.81	–23.12	–9.61		32.35	41.13	40.38

Note: Experimental values hold for equilibrium mixtures of conformers.

$P_{i,i+1}$, $P_{i,i+2}$, etc. Equation (1) is the key equation of many empirical schemes. Such schemes are only applicable to either small molecules or large molecules in the *trans* conformation, for which $P_{ij} = P_{i+k,j+k}$ (k is some displacement along the chain of the molecule), and all contributions starting with $P_{i,i+4}$ can be ignored. For the other conformers, we should, however, determine the dependence of P_{ij} on the mutual arrangement of fragments i and j, because, in compact conformations, fragments situated far apart along the chain may be spatially close to each other. There are no plausible approximations for handling such situations, but the RISM method allows the difficulty to be overcome. In what follows, we assume that the thermodynamic characteristics calculated by the RISM method give approximate estimates of the P_{ii} and P_{ij} contributions corresponding to interaction between closely spaced fragments. The exact P value can then be written in the form

$$P = P_{\text{RISM}} + \sum_i \Delta P_{ii} + \sum_i \sum_j \Delta P_{ij}, \qquad (2)$$

where P_{RISM} is the value of property P calculated by the RISM method, and ΔP_{ii} and ΔP_{ij} are the empirical parameters equal to the errors of P_{ii} and P_{ij} determination. To minimize the number of such parameters, it is assumed that hydrocarbon molecules comprise quasi-atoms C (modeling CH_n groups), all CC bonds have equal lengths, and all bond angles are also equal. Clearly, we then have

$$P_{ii} = P_{jj} = \alpha,$$
$$P_{i,i+1} = P_{j,j+1} = \beta,$$
$$P_{i,i+2} = P_{j,j+2} = \gamma,$$

etc. For linear C_nH_{2n+2} molecules, equation (2) becomes

$$\begin{aligned} P(n) &= n\alpha + (n-1)\beta + (n-2)\gamma + \ldots \\ &= P_{\text{RISM}} + n\Delta\alpha + (n-1)\Delta\beta + (n-2)\Delta\gamma. \end{aligned} \qquad (3)$$

It may seem that not all P_{ii} values are equal, and the assumption $P_{ii} = P_{jj} = \alpha$ is inaccurate. However, clearly, the transition from methane to ethane and other hydrocarbons can be described by the chemical reaction

$$CH_4 + CH_4 \longrightarrow C_2H_6 + H_2.$$

Therefore,

$$C_2H_6 = 2CH_4 - H_2.$$

For the transition from methane to propane, we have

$$CH_4 + CH_4 + CH_4 \longrightarrow C_3H_8 + 2H_2$$

and

$$C_3H_8 = 3CH_4 - 2H_2.$$

Generally, $C_nH_{2n+2} = nCH_4 - (n-1)H_2$. Formula (3) displays these considerations.

The $\Delta\alpha$, $\Delta\beta$, and $\Delta\gamma$ parameters are estimated by the method of least squares from the experimental data on a small set of molecules. The $\Delta G°$ values calculated by (3) for several hydrocarbon molecules are listed in Table 2. With $s = 1.79$, the $\Delta G°$ value for methane is reproduced very accurately, and, therefore, $\Delta\alpha \simeq 0$. To summarize, the use of (3) for calculating the total thermodynamic values by the RISM method makes it possible to accurately estimate $\Delta G°$ for linear hydrocarbon molecules.

Next, consider data on branched hydrocarbon molecules. Although their structures are more compact than those of *trans* conformers, their experimental $\Delta G°$ values are increased in comparison with linear hydrocarbons. RISM calculations with $s \neq 1$ predict the opposite trend. Some data on branched and isoelectronic linear hydrocarbons are included in Table 3. Note that the differences in $\Delta G°$ between *trans* conformers and the corresponding $(CH_3)_3C–R$ isomers are close to each other and can be considered equal for R of different lengths to within ±0.25 kcal/mol. It follows that obtaining good $\Delta G°$ estimates for branched isomers requires the introduction of corrections for branching; that is, the P value of some characteristic should be calculated by the equation

$$P = P_{RISM} + n\Delta\alpha + n_{1\cdots2}\Delta\beta + n_{1\cdots3}\Delta\gamma + \Delta_{branch}, \quad (4)$$

where $n_{1\cdot\cdot2}$ and $n_{1\cdot\cdot3}$ are the numbers of contributions corresponding to the $1\cdot\cdot2$ and $1\cdot\cdot3$ interactions, respectively. With the $\Delta\alpha$, $\Delta\beta$, and $\Delta\gamma$ parameters selected earlier, the introduction of the additional Δ_{branch} parameter makes it possible to obtain satisfactorily accurate estimates of $\Delta G°$. Several examples are given in Table 4. Unfortunately, there is no data on other molecules of this type. A similar approach can be applied to $(CH_3)_2CH–R$ isomers, for which Δ_{branch} parameters will be different.

In conclusion, consider data on cyclic hydrocarbon molecules given in Table 5. According to this table, RISM calculations qualitatively correctly reproduce the dependence of $\Delta G°$ on the number of C atoms (exceptions are the results on pentane and cyclopentane obtained with $s = 2$ and 1.79). It should, however, be taken into consideration that, according to (3),

$$P = P_{RISM} + n\Delta\alpha + (n-1)\Delta\beta + (n-2)\Delta\gamma,$$

for normal hydrocarbons and

$$P = P_{RISM} + n\Delta\alpha + n\Delta\beta + n\Delta\gamma, \quad (5)$$

for cyclic molecules; the $\Delta G°$ values for the latter should therefore be corrected by $\Delta\beta + 2\Delta\gamma$. The intro-

Table 2. Estimates of $\Delta G°$ for some hydrocarbons according to (4) (kJ/mol)

Molecule	Expt. [9]	$s = 1$	$s = 2$	$s = 1.79$
CH_4	8.40	8.40	8.40	8.40
C_2H_6	7.69	8.28	8.19	8.19
C_3H_8	8.19	7.11	7.98	7.86
C_4H_{10}	8.73	9.15	8.32	8.40
C_5H_{12}	9.78	9.95	9.66	9.70
C_6H_{14}	10.45	10.12	10.49	10.53
C_7H_{16}	10.99	11.12	11.12	11.20
C_8H_{18}	12.08	12.16	12.00	12.08

Note: $s = 1$: $\Delta\alpha = -27.92 \pm 0.20$, $\Delta\beta = 12.75 \pm 0.42$, $\Delta\gamma = -2.75 \pm 0.26$; $s = 2$: $\Delta\alpha = 3.39 \pm 0.20$, $\Delta\beta = -5.25 \pm 0.42$, $\Delta\gamma = 0.31 \pm 0.26$; $s = 1.79$: $\Delta\alpha = 0.042 \pm 0.43$, $\Delta\beta = -3.72 \pm 0.90$, $\Delta\gamma = 0.26 \pm 0.56$.

Table 3. Estimates of $\Delta G°$ for some linear and isoelectronic branched molecules (kJ/mol)

Molecule	Expt. [9]	$s = 1$	$s = 2$	$s = 1.79$
n-C_5H_{12} t	9.78	106.84	12.67	23.62
$C(CH_3)_4$	10.49	108.81	–23.12	–9.61
n-C_6H_{14} t	10.45	124.90	15.05	27.88
$(CH_3)_3C–C_2H_5$	10.87	124.73	–21.49	–6.35
n-C_7H_{16} t		143.83	17.18	31.98
$(CH_3)_3C–C_3H_7$		144.46	–17.81	–0.92
n-C_8H_{18} t		162.48	17.64	34.99
$(CH_3)_3C–C_4H_9$ t		164.69	–15.63	3.14

Table 4. Estimates of $\Delta G°$ for $C(CH_3)_4$ and $(CH_3)_3C–C_2H_5$ (kJ/mol)

Molecule	Expt. [9]	$s = 1$, $\Delta = 7.98$	$s = 2$, $\Delta = 35.95$	$s = 1.79$, $\Delta = 33.57$
$C(CH_3)_4$	10.49	11.66	10.62	10.78
$(CH_3)_3C–C_2H_5$	10.87	9.70	10.74	10.58

Table 5. Estimates of $\Delta G°$ for linear and cyclic hydrocarbons (kJ/mol)

Molecule	Expt. [9]	$\Delta\Delta G°$	$s = 1$	$\Delta\Delta G°$	$s = 2$	$\Delta\Delta G°$	$s = 1.79$	$\Delta\Delta G°$
n-C_5H_{12}	9.78		106.84		12.67		23.62	
C_5H_{10}	5.06	4.72	94.59	12.25(4.99)	13.79	−1.13(3.49)	23.62	0(3.22)
n-C_6H_{14}	10.45		124.90		15.05		27.88	
C_6H_{12}	5.18	5.69	107.55	13.17(6.42)	14.05	1.00(5.62)	25.29	2.59(5.81)

Notes: At equal numbers of C atoms, the contribution of ring closure is $\Delta\Delta G° = \Delta G°_{\rm norm} - \Delta G°_{\rm ring}$; given in parentheses are values corrected for $\Delta\beta + 2\Delta\gamma$ according to (5).

duction of these corrections improves the situation, and all $\Delta G°$ values for cyclic molecules become smaller than $\Delta G°$ for the corresponding normal hydrocarbons.

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