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EVALUATION OF THERMODYNAMIC FUNCTIONS RELATIVE TO CAVITY FORMATION IN AQUEOUS SOLUTIONS

Comparison of the results calculated from Scaled Particle Theory and Sinanoglu's theory for 2-alkyl-9-methyladenines

W. Zielenkiewicz, P. Zielenkiewicz[1] *and P. V. Lapshov*[2]

Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw
ul. Kasprzaka 44/52, Poland
[1]Institute of Biochemistry and Biophysics, Polish Academy of Sciences, 02-106 Warsaw
ul. Pawińskiego 5A, Poland
[2]Institute of Non-Aqueous Solution Chemistry, Russian Academy of Sciences
1 Akademicheskaja str., Ivanovo, Russia

Abstract

The results of calculation of free Gibbs energy and enthalpy of cavity formation were described using the Scaled Particle and Sinanoglu's theories.

Keywords: 2-alkyl-5-methyladenine, enthalpy of cavity formation, enthalpy of interaction

Introduction

The applications of the Scaled Particle Theory SPT [1–3] in the thermodynamic works are move and move abundant for calculation of Gibbs energies, entropies and enthalpies of cavity formation in various solvents [4–9]. The cavity terms calculated from SPT have also been compared [10] with those obtained from macroscopic theory of Sinanoglu ST [11, 12] and discrepancy between both sets of results was evident. In each of the theories the results depend to high extent on the accepted assumptions, parameters and algorithms used. Morel-Desrosiers and Morel [10] underlined the tremendous importance of knowing the diameter of solvent molecules with good accuracy in the evaluation of thermodynamic functions using SPT method. Zielenkiewicz *et al.* [13] announced the discrepancy between the results obtained in determination of the enthalpy of cavity formation using Sinanoglu's theory related with the use of various methods of determination of water surface accessible area S. For instance, the S value calculated for 9-methyladenine by method of Lavery *et al.* [14] corresponds to $77.7 \cdot 10^{-16}$ cm^2, whereas by the Finney method it is

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$165.5\cdot 10^{-16}$ cm^2 [15]. Consequently differ the thermodynamic parameters of cavity formation calculated by these two methods of calculation.

We are interested in the determination of thermodynamic properties of nucleic acid bases and its alkylated derivatives, particularly enthalpies of interaction,. $\Delta H^{\circ}_{\text{int}}$, of these compounds with its aqueous environment. This last value is derived from experimentally determined the enthalpies of sublimation, $\Delta H^{\circ}_{\text{sub}}$, and the enthalpies of solution, $\Delta H^{\circ}_{\text{sol}}$, and evaluated value of the enthalpy of cavity formation, $\Delta H^{\circ}_{\text{cav}}$. The reasonable selection of the method of calculation of $\Delta H^{\circ}_{\text{cav}}$ is of great interest. The calculations of $\Delta H^{\circ}_{\text{cav}}$ for a series of 2-alkyl-9-methyladenines presented here are dedicated to this goal.

SPT theory

According to SPT formalism, creation of a cavity in solvent capable of accommodating solute molecule is characterized by reversible work *W*, the value of which is dependent on the cavity size, solvent density and the temperature.

According to SPT the free energy of cavity is given by relation:

$$\Delta \text{G}_{\text{cav}} = K_{\text{o}} + K_1 r + K_2 r^2 + K_3 r^3$$

where

$$K_{\text{o}} = RT\left\{-\ln(1-y) + \frac{9}{2}\left(\frac{y}{1-\text{y}}\right)^2\right\} - \frac{N\Pi\delta_1^3 P}{6}$$

$$K_1 = \frac{RT}{\delta_1}\left\{6\left(\frac{y}{1-y}\right) + 18\left(\frac{y}{1-y}\right)^2\right\} + N\Pi\,\delta_1^2 P$$

$$K_2 = \frac{RT}{\delta_1^2}\left\{12\left(\frac{y}{1-y}\right) + 18\left(\frac{y}{1-y}\right)^2\right\} - 2\,N\Pi\delta_1 P$$

$$K_3 = \frac{4}{3}N\Pi P$$

and the enthalpy of cavity formation corresponds to:

$$\Delta H_{\text{cav}} = \alpha RT^2\left(\frac{y}{1-y}\right)\cdot\left(\frac{6B}{1-y} + \frac{36yD}{(1-y)^2} + 1\right)$$

where

$$B = 2\left(\frac{r}{\delta_1}\right)^2 - \frac{r}{\delta_1}$$

$$D = \left(\frac{r}{\delta_1}\right)^2 - \frac{r}{\delta_1} + \frac{1}{4}$$

R being the gas constant; T – temperature / K; P – pressure; $y = M\delta_1^3\gamma/6$ – packing coefficient; $\gamma = N/V$; N – Avogadro number; V – molar volume of the liquid; α – thermal expansion coefficient of the cavity; $\rho = (\delta_1 + \delta_2)/2$; δ_1 – the diameter of hard sphere of the solvent and δ_2 of the solute, respectively.

Sinanoglu theory

Sinanoglu theory, based on thermodynamic properties of pure liquids and dilute solutions, expresses the Gibbs energy of cavity formation by the relation:

$$\Delta G_{\mathrm{cav}} = K_1^e S\gamma(1 - X)$$

where

$$X = \left(1 - \frac{K_1^s}{K_1^e}\right)\left\{\frac{\partial \ln\gamma}{\partial \ln T} + \frac{2}{3}\alpha T\right\}$$

and the enthalpy of cavity formation $\Delta H^\circ_{\mathrm{cav}}$ by formula:

$$\Delta H^\circ_{\mathrm{cav}} = KS\gamma\left\{1 - \frac{\partial \ln\gamma_1}{\delta \ln T} - \frac{2}{3}\alpha_1 T\right\}$$

where: S – surface accessible area; γ – surface tension; α – coefficient of thermal expansion; T – temperature. The K_1^e and K_1^s are the constants adjusting the planar surface energy and entropy to highly curved microscopic dimensions. The constants K_1^e and K_1^s can be calculated from the empirical formula:

$$K_1 = 1 + \left(\frac{V_1}{V_2}\right)^{2/3}[K_1(1) - 1]$$

where K_1 corresponds either to K_1^e or K_1^s, V_1, V_2 – molecular van der Waals volumes of the solvent and solute, respectively; K_1^e [1], K^s [1] – factors for the pure solvent. According to [12], K_1^e [1] and K_1^s [1] for H_2O correspond to 1.277 and 1.235, respectively.

Results and discussion

The calculations of Gibbs energy and enthalpy of cavity formation, according to SPT theory, were made using the program CAVITY, elaborated by Kulikov and Lapshov (unpublished). The diameters of hard sphere of solutes were calculated from molecular volumes V_2 [17] according to the program GEPOL version 12 [17]. Surface accessible areas were calculated by Lavery method [14]. The calculation were based on the crystallographic data of crystalline compounds. The geometry of solutes was generated using the mean values for bond lengths and angles from compiled crystallographic databases [18, 19]. Hydrogen atoms were added assuming C–H distance of 1.09 Å and tetrahedral bond angles. Cartesian coordinates were obtained using EUKLID (Quantum Chemistry Exchange Program N-452, Indiana University).

The following constants were adopted [10] for the calculations:

$$\delta_1 = 2.75\ \text{Å};\ V_1 = 18.0687\ \text{cm}^3\cdot\text{mol}^{-1};\ \alpha = 2.57\cdot10^{-4}\ \text{K}^{-1};$$

$$\gamma = 72.00\ \text{dyn}\cdot\text{cm}^{-1};\ \delta\gamma/\delta T = -0.157\ \text{dyn}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}.$$

The results of calculations of V_2, S, ΔG_{cav} and ΔH_{cav} are collected in the Table 1 for following compounds: 9-methyladenine (m^9Ade), 2,9-dimethyladenine ($m_2^{2,9}$Ade), 2-ethyl-9-methyladenine (e^2m^9Ade), 2-propyl-9-methyladenine (p^2m^9Ade), 2-butyl-9-methyladenine (b^2m^9Ade).

Table 1 Molecular volumes V_2, surface accessible areas, ΔG_{cav} and ΔH_{cav} calculated from SPT and Sinanoglu methods

9-methyl-alkyladenines	S	V_2	SPT		Sinanoglu	
			ΔG_{cav} /	ΔH_{cav} /	ΔG_{cav} /	ΔH_{cav} /
			kJ·mol^{-1}			
9-methyladenine	77.2	116.7	48.7	7.9	36.9	58.5
2,9-dimethyladenine	84.8	133.4	52.6	8.6	40.8	64.6
2-ethyl-9-methyladenine	91.4	150.4	56.5	9.3	43.6	69.2
2-propyl-9-methyladenine	95.2	160.2	58.7	9.7	45.3	71.8
2-butyl-9-methyladenine	104.8	183.5	62.6	10.5	49.1	78.0

The results obtained are clearly different between the two theories. The values presented here constitute a quantitative illustration of conclusions formulated by Morel-Desrosiers and Morel when examining the course of function $\Delta H_{cav} = f(\delta_2)$, $\Delta G_{cav} = f(\delta_2)$ for different solvents, including water.

Comparison of ΔH_{cav} and ΔG_{cav} values obtained from Sinanoglu formalism shows that $\Delta G_{cav} << \Delta H_{cav}$ whereas the ΔG_{cav} values from SPT theory are higher than ΔH_{cav}. This implies different signs for the entropic contribution to the cavity formation. When using SPT theory as a reference one should say that Sinanoglu theory in general underestimates the entropic contribution. Further and more systematic investigations, involving also the dependence of results on parameters used, are necessary to verify generality of conclusion presented here.

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Zusammenfassung — Mittels der zitierten Theorien wurden die Resultate der Berechnung der freien Gibbs'schen Energien und Enthalpien für die Hohlraumbildung beschrieben.