

GAS PHASE AND LIQUID PHASE HYDRATION OF METHANOL: ENTHALPY AND ENTROPY CALCULATIONS

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The PCILO method was used to calculate interaction energies between methanol and water molecules. PCILO, CNDO/2 and *ab initio* (STO-3G) interaction energies for related processes were compared. Simple statistical thermodynamic calculations were performed for the formation of water-methanol complexes in the gas phase; $\text{CH}_3\text{OH}(\text{g}) + n \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH} \cdot n \text{H}_2\text{O}(\text{g})$, $n = 1, 3, 6$. It has been shown that the complete first solvation shell in the complex consists of six water molecules. To describe dissolution of methanol in water the cavity concept was used, making it possible to estimate the Henry law constant.

Partitioning between gas and liquid phases is of fundamental importance in chromatography and in various aspects of chemical engineering and industrial toxicology. The hydration of non-polar groups (hydrophobic hydration) represents the simplest of the so called hydrophobic interactions. The fundamental importance of these interactions has been discovered only recently¹.

METHODS AND CALCULATIONS

Having made an extensive analysis of various empirical, semiempirical and non-empirical methods², we decided to use the PCILO method³ for the following reasons: a) it has been successfully used to predict stabilization energies of hydrogen-bonded complexes⁴, b) it is superior to CNDO and INDO types of calculations as far as weak intermolecular interactions are concerned², c) the extremely high efficiency of the PCILO computational scheme facilitates calculations even on very extensive complexes.

The statistical thermodynamic model⁵ employs rigid-rotor clusters performing small-amplitude harmonic vibrations. The success of this approximation^{6,7} with water molecule clusters suggests its applicability to $\text{CH}_3\text{OH} \cdot n \text{H}_2\text{O}$ systems. PCILO interaction energies and optimal cluster geometries were obtained in a straightforward way and the latter used for evaluation of rotational partition functions⁵. It was much more complicated to obtain the vibrational frequencies. Even though we confined

ourselves to calculations of intermolecular vibrational normal frequency modes, ω_i , the dimension of the vibrational problem with the $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ cluster amounted to $6n$. This prompted us to employ the intermolecular vibrational frequencies proposed by Owicki and coworkers⁶. The intramolecular vibrational normal mode frequencies of the components of complexes under study were set equal to frequencies of free water and methanol molecules and therefore they canceled in the statistical thermodynamic treatment.

The statistical thermodynamic calculations concern formation of gas phase water-methanol complexes:



Owing to the assumption made, the following relationship between the $\Delta E_{\text{int}}^{(n)}$ energy and zero-point energy $\Delta H_0^{0(n)}$, of the processes (1) is valid

$$\Delta H_0^{0(n)} = \Delta E_{\text{int}}^{(n)} + \frac{1}{2}h \sum_{i=1}^{6n} \omega_i \quad (2)$$

Knowledge of the structure and energetics of the $\text{CH}_3\text{OH}\cdot n \text{H}_2\text{O}$ clusters also enables us to use the cavity concept introduced by Eley⁸, in the form developed by Pierotti^{9,10}, based on the scaled particle theory, for dissolution studies of gaseous methanol in liquid water. The process is characterized by K_{H} , the Henry law constant:

$$K_{\text{H}} = p_{\text{CH}_3\text{OH}}/x_{\text{CH}_3\text{OH}} \quad (3)$$

where $p_{\text{CH}_3\text{OH}}$ is the equilibrium pressure of methanol over the solution, and $x_{\text{CH}_3\text{OH}}$ is the mole fraction of methanol in water. This constant (3) can be expressed according to Pierotti¹⁰ in the following way

$$\ln K_{\text{H}} = G_c/RT + G_i/RT + \ln(RT/V), \quad (4)$$

where G_c and G_i are the partial molar Gibbs free enthalpies for the creation of a cavity in the solvent and for interaction of a solute molecule in the cavity with the surrounding solvent molecules, V is the molar volume of the solvent. Partial molar enthalpy and entropy for cavity formation, H_c and S_c , were calculated as described in ref.¹⁰ using core-diameter of water¹⁰, $\sigma_{\text{H}_2\text{O}} = 0.275$ nm. For the core-diameter of methanol we have selected the diameter of the molecule obtained from the density of fluid molecules (0.504 nm). The value of 0.370 nm, recently recommended by Pierotti¹¹, was tested too. The value of partial molar enthalpy, H_i , associated with interaction was taken from PCILO calculations. The cavity considered was represented

by a shell of water molecules obtained by PCILO optimization of geometry of the $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ complexes. Parallel with H_i and S_i calculation according to Pierotti¹⁰ (partial molar entropy of interaction S_i is according to ref.¹⁰ equal to zero) we attempted to improve the values by considering vibrational motion of the methanol molecule in the water cavity. For this purpose we used the above mentioned values of harmonic vibrational frequencies proposed by Owicki and coworkers⁶ for intermolecular vibrations in water dimer. Corresponding contributions to the H_i and S_i terms were evaluated in terms of the partition function of the harmonic oscillator.

RESULTS AND DISCUSSION

Energy and geometry of the $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ complexes. Mutual orientation of subsystems in the complex was found by minimization of the PCILO energies. Energy and geometry characteristics of three 1 : 1 complexes (Fig. 1) are given in Table I. The differences in ΔE for hydration of the polar (OH) and non-polar

TABLE I
Characteristics of 1 : 1 Complexes of the Methanol...Water

Type of complex ^a	$-\Delta E$, kJ/mol	r , nm ^a
<i>a</i>	18.42	0.265
<i>b</i>	16.61	0.265
<i>c</i>	4.724	0.306

^a See Fig. 1.

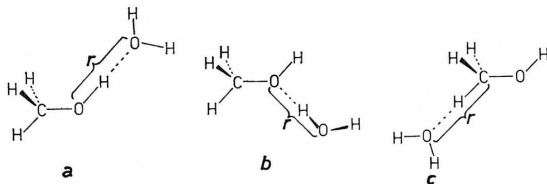


FIG. 1

Structure of the 1 : 1 Methanol...Water Complexes

(CH₃) part of methanol are large, which is, of course, in accordance with chemical intuition. Nevertheless, it is desirable to compare the numerical results with published nonempirical data. The most stable configuration of the CH₃OH...H₂O complex determined¹² by *ab initio* SCF calculations with an STO-3G basis set is that depicted in Fig. 1a ($r = 0.271$ nm, $\Delta E = -26.2$ kJ/mol). Hydration of methanol at CH₃ has not yet been studied theoretically; therefore we used published data on the methane...water complex. The computations^{13,14} carried out with the STO-3G and with the DZ basis sets both predict the same equilibrium structure possessing linear C—H...O hydrogen bond. The characteristics of the complex obtained with these bases are given in parentheses (r : 0.327, 0.385 nm; ΔE : -3.3, -2.1 kJ/mol). It is clear that PCILO stabilization energies are in fair agreement with the results of nonempirical calculations.

Models of methanol hydrated by three water molecules at CH₃ and OH are given in Fig. 2; the stabilization energies and intersystem separations are summarized in Table II. The data were obtained by optimization of all intersystem coordinates

TABLE II
Characteristics of the 1 : 3 Complexes of Methanol...Water

Complex ^a	$-\Delta E$, kJ/mol	r , nm ^b
CH ₃ OH...3 H ₂ O	52.23	0.265
HOCH ₃ ...3 H ₂ O	10.43	0.305

^a All O...O and all C...O distances are equal; ^b See Fig. 2.

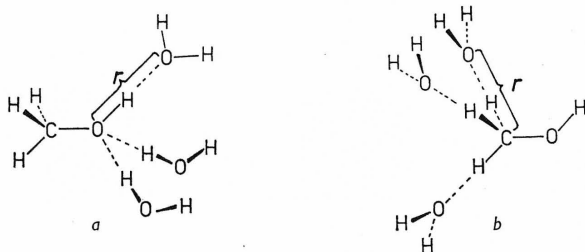


FIG. 2
Structure of the 1 : 3 Methanol...Water Complexes

of the respective complex. If we simply sum the pair stabilization energies of water and methanol we obtain -51.32 kJ/mol and -13.29 kJ/mol for the hydration of the polar and nonpolar end, respectively. It is seen from comparison of these values with those obtained by direct calculation for complexes with three water molecules (Table II), that in the former case the interaction of the three water molecules in the shell is slightly attractive (-0.91 kJ/mol), while in the latter case it is repulsive (2.86 kJ/mol). Even more pronounced interaction among water molecules in the shell was found in the case of methanol hexahydrate. In Fig. 3 the optimal structures of the staggered and eclipsed forms of methanol hexahydrate are depicted; Table III contains characteristics of both complexes. It should be pointed out that the hydration shell consisting of six water molecules is complete. Introduction of the seventh water molecule into the shell reduces interaction energy. On the other hand introduction of the water molecule into the second hydration shell leads to a small gain in interaction energy (about -0.42 kJ/mol).

TABLE III

Characteristics of the 1 : 6 Methanol...Water Complex

Complex ^a	ΔE , kJ/mol	r , nm ^b	
		O...O	C...O
CH ₃ OH (staggered)...6 H ₂ O	-65.07	0.265	0.305
CH ₃ OH (eclipsed)...6 H ₂ O	-68.54	0.265	0.305

^a See Fig. 3; ^b All O...O and all C...O distances are equal; see Fig. 3.

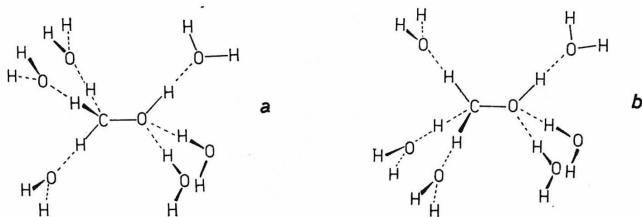


FIG. 3

Staggered (a) and Eclipsed (b) Forms of Methanol Hydrated by Six Water Molecules

Let us briefly discuss the data given in Table III. The larger stabilization energy of the eclipsed form is caused by larger attractive interaction of water molecules in the respective shells (eclipsed form -5.309 kJ/mol, staggered form -1.866 kJ/mol). A similar conclusion, *i.e.* stabilization of the eclipsed form of methanol owing to the interaction of water molecules in the shell was reached in ref.¹⁵. The authors attributed the effect to a sterically crowded arrangement of water molecules in the shell surrounding the eclipsed form of methanol. It has to be kept in mind, however, that the semi-empirical CNDO/2 method used is known to overestimate stabilization energies and underestimate intersystem separations. In the particular case, the CNDO/2 stabilization energy for the $\text{CH}_3\text{OH}\cdots 6 \text{H}_2\text{O}$ complex is about double the PCILO value, the O...O and C...O distances being about 0.01 nm shorter than the PCILO

TABLE IV

Thermodynamic Characteristics of the Gas Phase Water...Methanol Association Equilibria
 $\text{CH}_3\text{OH}(\text{g}) + n \text{H}_2\text{O}(\text{g}) = \text{CH}_3\text{OH}\cdot n \text{H}_2\text{O}(\text{g})$

Association process ^a	$\Delta E_{\text{int}}^{(n)}$ kJ/mol	$\Delta H_0^{0(n)}$ kJ/mol
$\text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$	-18.42	- 8.226
$\text{CH}_3\text{OH} + 3 \text{H}_2\text{O} = \text{CH}_3\text{OH}\cdot 3 \text{H}_2\text{O}$	-52.23	-19.60
$\text{CH}_3\text{OH} + 6 \text{H}_2\text{O} = \text{CH}_3\text{OH}\cdot 6 \text{H}_2\text{O}$	-68.54	- 1.222

^a From all possible processes dealing with various isomeric structures $\text{CH}_3\text{OH}\cdot n \text{H}_2\text{O}$ characteristics of those with the highest $|\Delta E_{\text{int}}^{(n)}|$ term are given; ^b Standard state is ideal gas phase at 1 atm

TABLE V

Thermodynamic Characteristics of Cavity Formation in Water (*c*) and Introduction of Methanol Molecule into the Cavity (*i*)

$\Delta H_{c,298.15}$ kJ/mol	$\Delta S_{c,298.15}$ J/mol/deg	$\Delta G_{c,298.15}$ kJ/mol	$\Delta E_{i,0}$ kJ/mol ^a
5.72 (3.32) ^b	-100.0 (-60.00) ^b	35.54 (21.21) ^b	- 8.226 (-18.42) ^c
			-41.13 (-51.33) ^c
			-53.03 (-63.23) ^c

^a $n = 1$ — the first line, $n = 3$ — the second line, $n = 6$ — the third line; ^b Cavity characteristics based on core diameter $\sigma_{\text{CH}_3\text{OH}} = 0.504$ nm (ref.¹⁰), the values in parenthesis on $\sigma_{\text{CH}_3\text{OH}} =$

values. Owing to larger distances between methanol and water molecules (resulting from the PCILO calculation), the water molecules in the shell are more separated. The closest approach between hydrogen and oxygen of two water molecules in the shell is 0.192 nm (ref.¹⁵), by CNDO/2, 0.254 nm by PCILO. The latter value seems plausible and therefore we cannot accept the tentative explanation¹⁵, based on steric crowding. It is apparent (Table III) that the staggered form of methanol is the most stable form for an isolated molecule in the gas phase, while in the hexahydrate the eclipsed form is preferred.

Statistical thermodynamic treatment. The treatment of the $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ clusters possessing the lowest $\Delta H_0^{0(n)}$ (i.e. for deepest energy minimum) was carried

$\Delta H_{298.15}^{0(n)}$ kJ/mol ^b	$\Delta S_{298.15}^{0(n)}$ J/mol/deg ^{b,c}	$\Delta G_{298.15}^{0(n)}$ kJ/mol ^b	$\log K_p^{(n)b,d}$
-10.41	-113.3 (76.4%)	23.36	-4.09
-27.54	-380.3 (80.5%)	85.84	-15.04
-18.49	-807.6 (92.9%)	222.3	-38.94

pressure; ^c In parenthesis relative contribution of the term $T|\Delta S_T^0|$ to the value of function $|\Delta H_T^0| + T|\Delta S_T^0|$ is given; ^d $\{K_p^{(n)}\} = (\text{atm})^{-n}$.

$\Delta H_{i,298.15}$ kJ/mol ^d	$\Delta S_{i,298.15}$ J/mol/deg	$\Delta G_{i,298.15}$ kJ/mol ^d
-0.494 (-18.42) ^c		-15.29 (-18.42) ^c
-33.40 (-51.33) ^c	49.62 (0.0) ^c	-48.19 (-51.33) ^c
-45.30 (-63.23) ^c		-60.10 (-63.23) ^c

= 0.370 nm (ref.¹¹); ^c Vibrational motion of methanol molecule in the cavity was neglected.

out for the given n . The intermolecular vibrational normal mode frequencies, ω_i , for the cluster $\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$ were identified with those⁶ of $(\text{H}_2\text{O})_2$, for the cluster $\text{CH}_3\text{OH}\cdot 3\text{H}_2\text{O}$ with those⁶ of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ and for the cluster $\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$ with those⁶ of $(\text{H}_2\text{O})_3$ (threefold). The values of standard thermodynamic characteristics for gas phase water-methanol equilibria (I) are given in Table IV. Thermodynamic characteristics of the cavity formation and interaction are presented in Table V. This table includes values calculated according to Pierotti¹⁰ and also by considering the vibrational motion of methanol molecule in the cavity. Interaction enthalpy is presented for each case studied, *i.e.* for $n = 1, 3$ and 6 .

The results presented in Table IV enabled us to estimate the gas phase stability of the $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ clusters ($n = 1, 3$ and 6). The three processes studied are controlled by the entropy term whose relative importance increases with the cluster size (Table IV). This result clearly illustrates the fundamental role of entropy in the region of weak intermolecular interactions. While according to the results presented in Table IV, the clusters $\text{CH}_3\text{OH}\cdot 3\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$ are completely unstable, the K_p value of the $\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$ complex indicates the possibility of its existence under ordinary pressure and temperature.

The results in Table IV are based only on characteristics of the cluster structures ($\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$) possessing the highest $|\Delta E_{\text{int}}|$ term. In principle, isomerism of these clusters ought to be considered in the sense of ref.¹⁶. Even though the phenomenon of cluster isomerism was ignored in calculations of data included in Table IV, we did not presume that this fact would qualitatively influence the prediction of cluster stability. Let us mention here, that in contrast to the case of pure water clusters⁶ all $\text{CH}_3\text{OH}\cdot n\text{H}_2\text{O}$ clusters considered in Table IV are nonchiral.

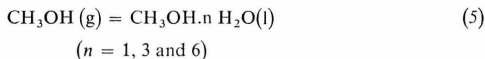
TABLE VI

Experimental and Theoretical Thermodynamic Characteristics of Gas Methanol Solution in Liquid Water (hydration)^a

Source	$\Delta H_{h,298.15}^0$ kJ/mol	$\Delta S_{h,298.15}^0$ J/mol/deg
Experiment ^c	-45.17 (-45.68)	-140 (-143)
PCILO, $n = 1$	2.93 (-15.00) ^d	-118.0 (-167.7) ^d
PCILO, $n = 3$	-29.97 (-47.90) ^d	-118.0 (-167.7) ^d
PCILO, $n = 6$	-41.87 (-59.80) ^d	-118.0 (-167.7) ^d
PCILO, total	-41.78 (-59.70) ^d	-117.6 (-167.3) ^d

^a Gas standard state: ideal gas at 1 atm pressure; solution standard state: solution at unit mole fraction; ^b Reciprocal value of the Henry's law constant: $\Delta G_{h,T}^0 = RT \ln K_H$; ^c Taken from refs.¹⁸

In contrast to the description of gas phase the values in Table IV are not directly applicable in the case of dissolution of methanol in liquid water. However, a satisfactory description of the latter process can be obtained by means of values of cavity and interaction terms presented in Table V. Those values served us for determination of molar heats (ΔH_h^0) and entropies (ΔS_h^0) of hydration in each case studied (Table VI). These values presented an important problem — isomerism of the cavities. The problem was how to assemble the contributions of the individual cavity forms proposed ($n = 1, 3$ and 6). Let us formulate the hydration equilibria according to the coordination number n as follows



and let us use for their description the partial equilibrium constants

$$1/K_H^{(n)} = x_{\text{CH}_3\text{OH} \cdot n \text{H}_2\text{O}} / p_{\text{CH}_3\text{OH}} \quad (6)$$

The equilibria (5) then represent a special simple case of the so called equilibria with isomerism of reaction components generally described in ref.¹⁶ and applied recently to the multimolecular clusters in ref.¹⁷. These results enabled us to assess the contributions of partial equilibria (5) to the values obtained by experiment. It is obvious that, for example, for the total Henry's constant the following equation holds in our case

$$1/K_H = 1/K_H^{(1)} + 1/K_H^{(3)} + 1/K_H^{(6)} \quad (7)$$

 ΔG_h^0
kJ/mol

 $1/K_H$
(atm⁻¹)^b

-3.517 (-3.144)	4.13 (3.56)
38.13 (34.99) ^d	2.09 · 10 ⁻⁷ (7.40 · 10 ⁻⁷) ^d
5.225 (2.091) ^d	1.22 · 10 ⁻¹ (4.30 · 10 ⁻¹) ^d
-6.679 (-9.812) ^d	1.48 · 10 ¹ (5.24 · 10 ¹) ^d
-6.699 (-9.833) ^d	1.49 · 10 ¹ (5.28 · 10 ¹) ^d

and ¹⁹ (in parenthesis); ^d Vibrational motion of methanol in the cavity is neglected.

Similar relations are easily obtainable for ΔH_h^0 , ΔS_h^0 and ΔG_h^0 according to the treatment in refs^{16,17}. Thus proper comparison of theoretical and experimental^{18,19} results is possible (Table VI). For the purpose of Table VI the values of H_c and S_c based on $\sigma_{\text{CH}_3\text{OH}} = 0.504$ nm have been used only. This value provides better agreement with experiment.

It can be seen from Table VI that the cavity with six-membered shell dominates the characteristics of the dissolution; the cases with $n = 1$ and 3 are negligible. The agreement with experiment is satisfactory, especially in the case where the values obtained by the original Pierotti treatment¹⁰ were corrected by considering the vibrational motion of methanol in the cavity. In the latter case the error in K_H is smaller by more than one order of magnitude. Let us mention that the use of properly calculated vibrational frequencies of $\text{CH}_3\text{OH} \cdot 6 \text{H}_2\text{O}$ instead of estimated values ought to improve the entropy term. It may be expected that the force constants are higher in $\text{CH}_3\text{OH} \cdot 6 \text{H}_2\text{O}$ than in water and that therefore the corresponding vibrational frequencies are higher than those used in this paper. It would indeed decrease the vibrational contribution to S_1 .

In spite of the numerical agreement obtained it should be stressed that the description of translation, rotation and vibration motions of dissolved molecules in solution is, from a theoretical point of view, too simplified. The observed agreement should rather be ascribed to the series of fortunately chosen approximations in the course of derivation of the cavity conception than to the level of sophistication of the cavity conception itself. However, the approach used is apparently the only statistical thermodynamic tool effectively applicable at present in connection with quantum chemical methods to the study of dissolution of gas in liquids.

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Note added in proof: Accurate values of the sums of the pair stabilization energies on the OH and CH₃ groups of methanol (−51·32 and −13·29 kJ/mol, p. 669) cannot be obtained from the data in Table I because in Table I (and also Table II) only energies of the most stable forms (*i. e.* either eclipsed or staggered) of the individual complexes are given. For example, the value of 2·86 kJ/mol (p. 669) was obtained as energy difference between −10·43 kJ/mol (HOCH₃ ... 3H₂O, eclipsed, Table II) and −13·29 kJ/mol (triple of the stabilization energy of HOCH₃ ... H₂O, eclipsed, not included in Table I).