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Association Constants of Methanol in Lattice Models†

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The association constants of methanol in the gas phase and in the dilute solution of a nonpolar solvent are calculated for a series of lattice models with the aid of the relations derived in the previous paper.¹ A detailed discussion is given and a comparison is made with the results of other statistical considerations.

1 INTRODUCTION

Although the lattice model cannot be treated as a good approximation to the liquid state, it is a helpful tool for examination of effects of excluded volume, specific interactions (i.e., hydrogen bonds), dispersion interactions between solute and solvent molecules, and comparison of flexible and rigid molecules. We have applied the lattice model to the calculation of association constants for models of aliphatic alcohol molecules.

In the preceding paper¹ we introduced the chemical equilibrium laws into the statistical description of the lattice model of a dilute aliphatic alcohol solution in a nonpolar solvent and we obtained the expressions for the association constants K_j^∞ , in units of dimensionless density. Thus

$$\begin{aligned} K_i^\infty &= \Gamma_i \eta^{(i)} \simeq \Gamma_i \eta & i = 2, 3, 4, \dots \\ K_{ic}^\infty &= \Gamma_{ic} \eta^{(i)} \eta_{iso}^{(i)} \simeq \Gamma_{ic} \eta^2 & i = 3, 4, \dots \end{aligned} \quad (1)$$

where index "c" refers to cyclic complexes, $\Gamma_i = g_i / (g_i - 1g_1)$, $\Gamma_{ic} = g_{ic} / (g_i - 1g_1)$, and $\eta^{(i)} = \exp(-\beta \epsilon^{(i)})$, $\eta_{iso}^{(i)} = \exp(-\beta \epsilon_{iso}^{(i)})$.

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Here $\varepsilon^{(i)}$ is the energy difference which corresponds to the formation of the successive linear complex A_i (solvated), $\varepsilon_{\text{iso}}^{(i)}$ is that which corresponds to the isomerization $A_i \rightleftharpoons A_{ic}$, g_k is the number of configurations of one molecule A_k (per one lattice site) and $\beta = 1/(kT)$. In the simplest case all $\eta^{(i)}$ are equal, also the energy of isomerization is of the same order of magnitude, so that $\eta_{\text{iso}}^{(i)} \simeq \eta$. In this case $\eta = \exp[-\beta(\varepsilon_{\text{OH}} + \varepsilon_{\text{II}} - \varepsilon_{\text{HI}} - \varepsilon_{\text{OI}})]$, where ε_{ij} denotes the interaction energy between "i" and "j" "contact points" (ε_{OH} represents the association interaction of alcohol, ε_{HI} and ε_{OI} represents the interaction between an alcohol and a solvent and ε_{II} represents between molecules of solvent). These contact energies have been introduced by Barker² many years ago.

In passing we mention that the attempts to calculate the association constants from statistical considerations are not numerous, the best-known example being that of Sarolea-Mathot³ (see however Refs. 4 and 5). In this paper, basing on formulae (1), we calculate for a number of lattice models the association constants of methanol. The influence of the chain length of the alcohol molecule, was discussed in the previous paper.¹















2 ASSOCIATION CONSTANTS OF METHANOL IN LATTICE MODELS OF SOLUTION IN NONPOLAR SOLVENT


We assume that a solvent molecule is a monomer occupying one lattice site. Then any configuration is in fact determined by the configuration of the solute molecules, the solvent merely filling the available holes. There is no need to average over the configurations of the solvent—a difficult task accomplished so far only in Monte Carlo simulations. The calculated values of the entropic contributions Γ_i and Γ_{ic} to the association constants K_i^∞ and K_{ic}^∞ are given in Table I. Table II contains the calculated values of K_j^∞ for an assumed value of η and Table III contains a description of the corresponding lattice models. In Table III we show models of monomers (one methanol molecule) and of dimers (two methanol molecules connected by the hydrogen bond); configurations of further successive complexes can be easily constructed by the same rules. Thus OH segments of two molecules must be nearest neighbours and must interact by the "H" and "O" contact points each alcohol molecule can form only one hydrogen bond with the hydrogen atom of a neighbouring molecule. The hydrogen bond is associated with an arrow and is directed from the "H" (acceptor) contact point to one of the allowed "O" (donor) contact points. These allowed "O" contact points differ from model to model as can be seen from Table III.


In the infinite dilute solution densities ρ_k go into mole fractions x_k and association constants expressed in mole fractions and in densities are equal

TABLE I

Entropic contributions to association constants of methanol-like molecules on the lattice.

No	The kind of model	Lattice	Γ_2	Γ_3	Γ_{3c}	Γ_4	Γ_{4c}
1a	The Barker model		$\frac{1}{2}$	$\frac{15}{32}$	0	$\frac{5}{12}$	$\frac{1}{480}$
1b			$\frac{2}{3}$	$\frac{247}{384}$	0	$\frac{1619}{2966}$	$\frac{27}{790}$
2a	The Sarolea model		$\frac{1}{8}$	$\frac{3}{4}$	0	$\frac{3}{4}$	0
2b			$\frac{1}{12}$	$\frac{5}{6}$	0	$\frac{5}{6}$	0
3a	Model A		$\frac{3}{4}$	$\frac{3}{4}$	0	$\frac{25}{36}$	$\frac{1}{72}$
3b			$\frac{5}{6}$	$\frac{23}{30}$	$\frac{1}{45}$	$\frac{35}{46}$	$\frac{1}{138}$
3c			$\frac{5}{6}$	$\frac{5}{6}$	0	$\frac{121}{150}$	$\frac{1}{150}$
4a	Model B		$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{1}{4}$	0
4b			$\frac{1}{6}$	$\frac{1}{6}$	0	$\frac{1}{6}$	0
4c			$\frac{1}{6}$	$\frac{23}{144}$	0	$\frac{2251}{14904}$	$\frac{1}{7452}$
5a	Model C		$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{5}{32}$	$\frac{1}{128}$
5b			$\frac{1}{6}$	$\frac{1}{8}$	$\frac{1}{72}$	$\frac{1}{6}$	0
5c			$\frac{1}{6}$	$\frac{1}{6}$	0	$\frac{59}{384}$	$\frac{1}{1536}$
6	Model D		$\frac{1}{3}$	$\frac{7}{24}$	$\frac{1}{144}$	$\frac{5}{21}$	$\frac{1}{336}$

 simple square lattice ($z = 4$)

 triangular lattice ($z = 6$)


 simple cubic lattice ($z = 6$)

TABLE II

Association constants of methanol-like molecules on the lattice, in units of dimensionless density $\rho = N/B$ ($t = 25^\circ\text{C}$, $\epsilon_{\text{OH}} = -19665 \text{ J/mol}^6$, $\epsilon_{\text{OI}} = \epsilon_{\text{HI}} = 0.2 \cdot \epsilon_{\text{OH}} = -3933 \text{ J/mol}$, $\epsilon_{\text{II}} = 0.1 \cdot \epsilon_{\text{OH}} = -1966 \text{ J/mol}$; $\eta = 258.1$).

No	K_2^∞	K_3^∞	K_{3c}^∞	K_4^∞	K_{4c}^∞
1a	129.1	121.0	0	107.5	138.8
1b	172.1	166.0	0	140.9	227.6
2a	32.26	193.6	0	193.6	0
2b	21.51	215.1	0	215.1	0
3a	193.6	193.6	0	179.2	925.2
3b	215.1	197.9	1480	196.4	482.7
3c	215.1	215.1	0	208.2	444.1
4a	64.53	64.53	0	64.53	64.53
4b	43.02	43.02	0	43.02	43.02
4c	43.02	41.22	0	38.98	8.939
5a	64.53	64.53	0	40.33	520.4
5b	43.02	32.26	925.2	28.68	0
5c	43.02	43.02	0	39.66	43.37
6	86.03	75.28	462.6	61.45	198.3

In all considered models, except for the Sarolea model, the successive linear association constants are equal or almost equal. *If we neglect the existence of cyclic associated structures we get the Mecke-Kempton model⁷ with all successive linear association constants (K_x) equal. In the Sarolea model³ the dimerization constant is by an order of magnitude less than the constant of the successive r -merization. The Sarolea reasoning leading to this conclusion, is as follows.*

One assumes first that one alcohol molecule occupies one site of a lattice of coordination number z and can rotate taking up $p_1 = z$ orientations of equal energy. Secondly the molecule linked by the hydrogen bond has only one of the $p_1 p_{i-1}$ possible orientations of two component molecules. From the equivalent of Eqs. (1), Sarolea obtained

$$\frac{K_2}{K} = \frac{1}{2(z-1)} \quad (2)$$

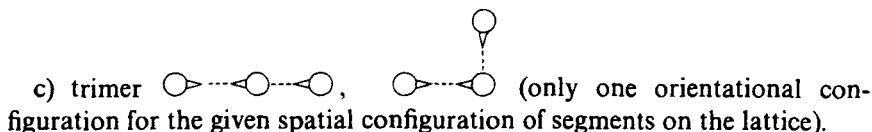
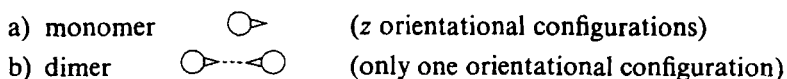
Indeed if $g_1 = p_1 = z$, K_2 contains a factor $(\frac{1}{2})z/z^2$, whereas K_3 contains a factor $[(\frac{1}{2})z(z-1)]/[(\frac{1}{2})z \cdot z]$. Thus $K_2/K_3 = 1/[2(z-1)]$. Similarly for $K_4 = K_3$, one would have

$$\frac{g_4}{g_3 g_1} = \frac{(\frac{1}{2})z(z-1)^2}{(\frac{1}{2})z(z-1)z} = \frac{z-1}{z}$$

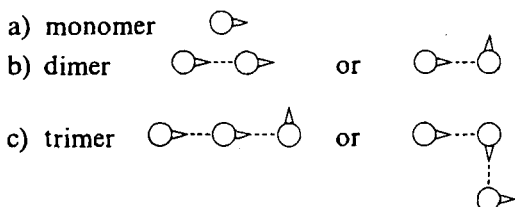
and

$$\frac{K_2}{K_4} = \frac{1}{2(z-1)}$$

The trouble is that these numbers correspond to a very special model of association, illustrated by the following pictures



It is easy to notice that such models of dimer and trimer are inconsistent. We can directly improve on the Sarolea model in the simplest way, constructing the model *A* (see Table III) in which one methanol molecule occupies also one lattice site, has also one association contact point and *z* possible orientations for the monomer. The successive complexes A_i in this model look as follows



In other words the hydrogen bond is directed (can be associated with an arrow)—an assumption conspicuously absent from the Sarolea model. Then

$$g_1 = z \quad g_2 = z(z - 1) \quad g_3 = z(z - 1)^2$$



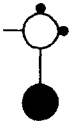
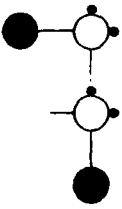







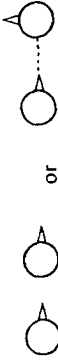


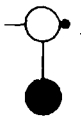
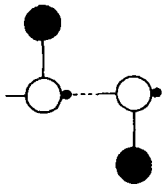


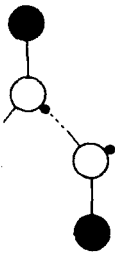
where one $(z - 1)$ factor always comes from the (assumed) $(z - 1)$ orientational configurations of the terminal segment. Therefore

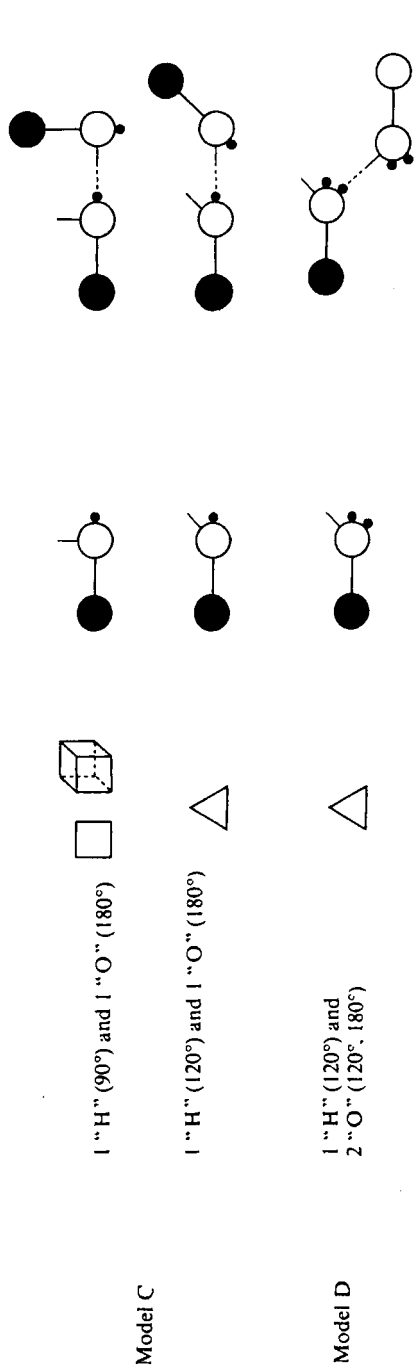
$$\frac{K_2}{K_3} = \frac{g_2 \cdot g_2 g_1}{g_1^2 \cdot g_3} = \frac{g_2^2}{g_1 g_3} = \frac{z^2(z - 1)^2}{z \cdot z(z - 1)^2} = 1$$

The ratio K_2/K_3 in the model *A* is exactly equal to unity. The assumption of Sarolea that the molecule linked by the hydrogen bond has only one of the $p_1 \cdot p_{i-1}$ possible orientations of two component molecules is well founded for the case of an *A - B* association (acetone-chloroform) discussed in the same paper.³ Next, it is necessary to take into account the cyclic structures. Then the total trimerization constant $K_3 = K_3^{\text{lin}} + K_3^{\text{cyc}}$, obtained from fitting the experimental data may give the ratio $K_2/K_3 < 0.2$, although $K_2/K_3^{\text{lin}} \approx 1$. In our model calculations (see Tables I and II) $K_2/K_3^{\text{lin}} = 1 - 1.3$ depending on the model, and $K_2/(K_3^{\text{lin}} + K_3^{\text{cyc}}) = 0.045 - 0.16$.

If the assumption of additivity of hydrogen bond energies in successive complexes A_k is made, we have in all equations (1) one energy factor η which

TABLE III
Description of models.

The kind of model	Association contact points	Lattice	Methanol monomer in two dimensions	Methanol dimer in two dimensions
The Barker model	1 "H" (90°) and (z - 2) "O"	 		
The Sarolea model	1 "association contact point"	 		
Model A	1 "association contact point"	 		
Model B	1 "H" and 1 "O" (both 90°)	 		
Model B	1 "H" and 1 "O" (both 120°)			



— "H" contact point.
 ● "O" contact point
 ▽ "association contact point"
 --- hydrogen bond.

All angles given in parentheses are referred to the direction of the C—O bond.

apart from small solvent effects is equal to $\exp(-\beta\epsilon_{\text{OH}})$. The recent quantum mechanical calculations indicate that the hydrogen bond energies are not strictly additive. Large differences were found for water complexes⁸ but for methanol molecules this nonadditivity is much smaller. Murthy *et al.*⁹ calculated that the hydrogen bond energy in linear methanol trimer (6.8 kcal per mol of hydrogen bonds) is a bit larger than that in a dimer (6.46 kcal). This correction can always be introduced into calculations of K_2 and K_3 . A more serious nonadditivity is expected for cyclic trimers. In the simplest picture an energy $3\epsilon_{\text{OH}}$ is evolved when a cyclic trimer dissociates into three monomers compared to $2\epsilon_{\text{OH}}$ evolved for a linear trimer. Then the isomerization constant for trimers should have an extra factor $\eta_{\text{iso}} \simeq \eta = \exp(-\beta\epsilon_{\text{OH}})$. Unfortunately we know of no quantum mechanical calculations which would tell us how much η_{iso} can differ from η . We hope perhaps to gain some insight from the detailed analysis of the recent excess heat capacity data¹⁰ in a very wide temperature range for the systems of propanol in hydrocarbons.

3 ASSOCIATION CONSTANTS OF METHANOL—LATTICE GAS MODEL

In the simple lattice models each segment of molecule occupies one lattice site and although the existence of the finite volume and the excluded volume of molecules is taken into account, we are very far from reality for real associating molecules. One can modify the simple lattice model by allowing the given molecule to occupy several neighbouring lattice sites, with the rules of occupation of sites, depending on the shape and size of the molecule. If we placed the given model of the molecule on a finer and finer lattice, we could more and more accurately take into account the real shape and size of the molecule by appropriately constructing the rules for occupation of sites and groups of sites.

We have tried to find a sufficiently fine lattice which could accommodate stereochemically a realistic model of the associating methanol molecule. In the case of alcohol molecules the lattice must fulfill the following conditions

a) ensure the real (approximately tetrahedral) angles between C—C—C and C—O—H bonds within molecule

b) specifically ensure the correct geometry of the hydrogen bonds: on alcohol molecule can form only one hydrogen bond with the hydrogen atom of a neighbouring molecule; this hydrogen atom lies on the bisector of the directions of two lone electron pairs on oxygen atom, and O---O---O angle ought to be about 120° (as proved most convincingly by the details of the crystallographic structure of solid methanol).¹¹

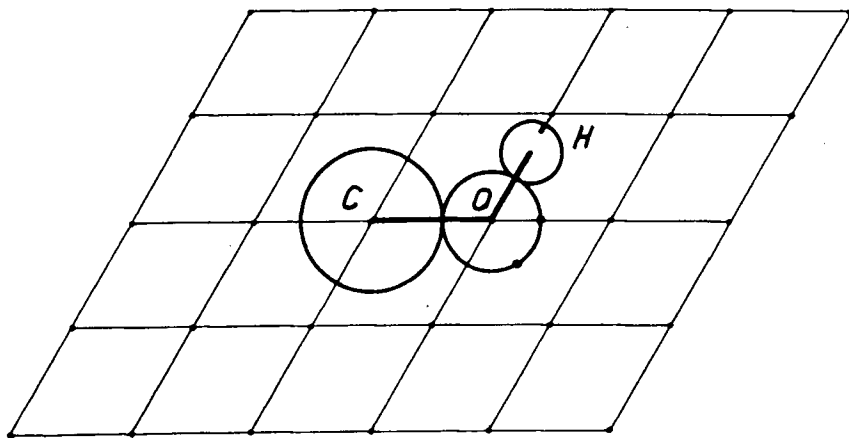


FIGURE 1 Model of methanol molecule on the hexagonal closed packed lattice: only one plane of lattice sites is shown, — denotes "H" contact point, ● denotes "O" contact point.

In addition, it would be an advantage, if cyclic trimers and tetramers (but not dimers) could be accommodated. We have found that on the hexagonal closed packed lattice ($z = 12$) a reasonable model of methanol could be constructed. In this model each methanol molecule is composed of two different segments. The first segment contains the methyl group, the other one contains the hydroxyl group so that the centers of the methyl group and the oxygen atom are on two nearest neighbour lattice sites (see Figure 1). Thus the nearest intersite distance is determined as equal to the length of the C—O bond (1.42 Å) and scales all other distances on the lattice. The hydroxyl segment has three association contact points: one "H" contact point in the direction of the O—H bond and two "O" contact points in specified locations on the O surface. One "O" contact point, situated along the C—O bond, takes part in cyclic complexes, the other one in linear complexes. Placing on the hexagonal closed packed lattice one methanol molecule gives the excluded volume of 140 lattice sites. The coordinations of the excluded lattice sites are summarised in Table IV; values of the van der Waals radii for methyl group and oxygen atom were adopted after Bondi¹² ($r_{\text{CH}_3} = 2.0 \text{ \AA}$, $r_{\text{O}} = 1.45 \text{ \AA}$) and the influence of hydrogen atom of hydroxyl group, as much smaller than the oxygen atom, on the volume exclusion is here neglected.

Taking into account these restrictions and conditions (a), (b) we calculated the combinatorial factors g_j . The corresponding numbers are

$$g_1 = 12, \quad g_2 = 192, \quad g_3 = 786, \quad g_{3c} = 16, \quad g_4 = 3072, \quad g_{4c} = 24.$$

TABLE IV

Excluded lattice sites after placing one CH₃OH molecule on hexagonal closed packed lattice (coords. of C atom (0, 0, 0), and O atom (1, 0, 0)).

Cartesian coordinates of lattice sites forbidden for CH₃ and OH segments of other molecules.

$(\pm 2, 0, 0), (-1, 0, 0), (\pm \frac{3}{2}, \pm \sqrt{\frac{3}{2}}, 0), (\pm \frac{1}{2}, \pm \sqrt{\frac{3}{2}}, 0), (\frac{3}{2}, \pm \sqrt{\frac{3}{2}}, 0), (\pm 1, \pm \sqrt{3}, 0), (0, \pm \sqrt{3}, 0),$
 $(\pm 2, 1/\sqrt{3}, \sqrt{\frac{3}{2}}), (\pm 1, 1/\sqrt{3}, \sqrt{\frac{3}{2}}), (0, 1/\sqrt{3}, \sqrt{\frac{3}{2}}), (\pm \frac{3}{2}, 5/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, 5/(2\sqrt{3}), \sqrt{\frac{3}{2}}),$
 $(\pm \frac{3}{2}, -1/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, -1/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\frac{3}{2}, -1/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\pm 1, -2/\sqrt{3}, \sqrt{\frac{3}{2}}),$
 $(0, -2/\sqrt{3}, \sqrt{\frac{3}{2}}), (2, -2/\sqrt{3}, \sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, -7/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\frac{3}{2}, -7/(2\sqrt{3}), \sqrt{\frac{3}{2}}),$
 $(\pm \frac{3}{2}, 1/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, 1/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (\frac{3}{2}, 1/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (\pm 1, 2/\sqrt{3}, -\sqrt{\frac{3}{2}}),$
 $(0, 2/\sqrt{3}, -\sqrt{\frac{3}{2}}), (2, 2/\sqrt{3}, -\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, 7/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (\frac{3}{2}, 7/(2\sqrt{3}), -\sqrt{\frac{3}{2}}),$
 $(\pm 2, -1/\sqrt{3}, -\sqrt{\frac{3}{2}}), (\pm 1, -1/\sqrt{3}, -\sqrt{\frac{3}{2}}), (0, -1/\sqrt{3}, -\sqrt{\frac{3}{2}}), (\pm \frac{3}{2}, -5/(2\sqrt{3}), -\sqrt{\frac{3}{2}}),$
 $(\pm \frac{1}{2}, -5/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (\pm \frac{3}{2}, 1/(2\sqrt{3}), 2\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, 1/(2\sqrt{3}), 2\sqrt{\frac{3}{2}}), (\pm 1, 2/\sqrt{3}, 2\sqrt{\frac{3}{2}}),$
 $(0, 2/\sqrt{3}, 2\sqrt{\frac{3}{2}}), (\pm 1, -1/\sqrt{3}, 2\sqrt{\frac{3}{2}}), (0, -1/\sqrt{3}, 2\sqrt{\frac{3}{2}}), (2, -1/\sqrt{3}, 2\sqrt{\frac{3}{2}}),$
 $(\pm \frac{3}{2}, -5/(2\sqrt{3}), 2\sqrt{\frac{3}{2}}), (\pm 1, 1/\sqrt{3}, -2\sqrt{\frac{3}{2}}), (0, 1/\sqrt{3}, -2\sqrt{\frac{3}{2}}), (2, 1/\sqrt{3}, -2\sqrt{\frac{3}{2}}),$
 $(\pm \frac{3}{2}, 5/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, -1/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, -1/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}),$
 $(\pm 1, -2/\sqrt{3}, -2\sqrt{\frac{3}{2}}), (0, -2/\sqrt{3}, -2\sqrt{\frac{3}{2}})$

Cartesian coordinates of lattice sites forbidden only for CH₃ segments of other molecules.

$(3, 0, 0), (-\frac{3}{2}, \pm \sqrt{\frac{3}{2}}, 0), (\pm 2, \pm \sqrt{3}, 0), (\pm \frac{1}{2}, \pm (\frac{3}{2})\sqrt{3}, 0), (-\frac{3}{2}, -1/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (3, 1/\sqrt{3}, \sqrt{\frac{3}{2}}),$
 $(\frac{3}{2}, 5/(2\sqrt{3}), \sqrt{\frac{3}{2}}), (\pm 1, 4/\sqrt{3}, \sqrt{\frac{3}{2}}), (0, 4/\sqrt{3}, \sqrt{\frac{3}{2}}), (-2, -2/\sqrt{3}, \sqrt{\frac{3}{2}}), (-\frac{3}{2}, -7/(2\sqrt{3}), \sqrt{\frac{3}{2}}),$
 $(-\frac{3}{2}, 1/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (-2, 2/\sqrt{3}, -\sqrt{\frac{3}{2}}), (-\frac{3}{2}, -7/(2\sqrt{3}), -\sqrt{\frac{3}{2}}), (3, -1/\sqrt{3}, -\sqrt{\frac{3}{2}}),$
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 $(2, 2/\sqrt{3}, 2\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, 7/(2\sqrt{3}), 2\sqrt{\frac{3}{2}}), (-2, -1/\sqrt{3}, 2\sqrt{\frac{3}{2}}), (\pm \frac{3}{2}, -5/(2\sqrt{3}), 2\sqrt{\frac{3}{2}}),$
 $(-2, 1/\sqrt{3}, -2\sqrt{\frac{3}{2}}), (\pm \frac{3}{2}, 5/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}), (\frac{3}{2}, -1/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}), (2, -2/\sqrt{3}, -2\sqrt{\frac{3}{2}}),$
 $(\pm \frac{1}{2}, -7/(2\sqrt{3}), -2\sqrt{\frac{3}{2}}), (\pm \frac{1}{2}, \pm \sqrt{\frac{3}{2}}, \pm \sqrt{6}), (\pm 1, 0, \pm \sqrt{6}), (0, 0, \pm \sqrt{6})$

For the case of lattice gas, formulae (1) change to the form

$$K_{pi} = \frac{g_i}{g_{i-1}g_1} \frac{v_0}{kT} \eta \quad (3)$$

$$K_{pic} = \frac{g_{ic}}{g_{i-1}g_1} \frac{v_0}{kT} \eta^2$$

where $v_0 \equiv V/B$ is a volume per one lattice site and for the hexagonal close packed lattice it is equal $d_0^3/\sqrt{2}$. The quantity d_0 is the nearest neighbour lattice site distance, equal the length of C—O bond (1.42 Å). Comparing relations (3) with relations (1) we have an extra term v_0/kT which is connected with passing from $K_p^\infty = K_x^\infty$ to K_p . Knowing v_0 and the g_j 's we can calculate association constants K_p ; the results for various assumed values of hydrogen bond energies are given in Table V.

TABLE V

Examples of association constants of methanol in the lattice gas multisite model in [atm⁻¹]

K_p [atm ⁻¹]	t	ϵ_{OH} [J/mol]					
		-12552	-16736	-20920	-23305	-25104	-29288
K_2	25°C	$6.57 \cdot 10^{-4}$	$3.55 \cdot 10^{-3}$	$1.92 \cdot 10^{-2}$	$5.03 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	$5.62 \cdot 10^{-1}$
	40°C	$4.91 \cdot 10^{-4}$	$2.45 \cdot 10^{-3}$	$1.22 \cdot 10^{-2}$	$3.05 \cdot 10^{-2}$	$6.09 \cdot 10^{-2}$	$3.04 \cdot 10^{-1}$
	100°C	$1.90 \cdot 10^{-4}$	$7.31 \cdot 10^{-3}$	$2.81 \cdot 10^{-3}$	$6.07 \cdot 10^{-3}$	$1.08 \cdot 10^{-2}$	$4.18 \cdot 10^{-2}$
	500 K	$5.07 \cdot 10^{-5}$	$1.39 \cdot 10^{-4}$	$3.80 \cdot 10^{-4}$	$6.74 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$	$2.84 \cdot 10^{-3}$
	1000 K	$5.81 \cdot 10^{-6}$	$9.60 \cdot 10^{-6}$	$1.59 \cdot 10^{-5}$	$2.04 \cdot 10^{-5}$	$2.63 \cdot 10^{-5}$	$4.34 \cdot 10^{-5}$
K_3	25°C	$6.57 \cdot 10^{-4}$	$3.55 \cdot 10^{-3}$	$1.92 \cdot 10^{-2}$	$5.03 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	$5.62 \cdot 10^{-1}$
K_{3c}	25°C	$2.16 \cdot 10^{-3}$	$6.33 \cdot 10^{-2}$	1.85	$1.27 \cdot 10^1$	$5.42 \cdot 10^1$	$1.58 \cdot 10^3$
K_4	25°C	$6.57 \cdot 10^{-4}$	$3.55 \cdot 10^{-3}$	$1.92 \cdot 10^{-2}$	$5.03 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	$5.62 \cdot 10^{-1}$
K_{4c}	25°C	$8.10 \cdot 10^{-4}$	$2.37 \cdot 10^{-2}$	$6.93 \cdot 10^{-1}$	4.50	$2.03 \cdot 10^1$	$5.92 \cdot 10^2$

The semiempirical literature values amount to $K_2 = 5.67 \cdot 10^{-2} \text{ atm}^{-1}$ (25°C)¹³, $K_3 = 4.69 \text{ atm}^{-1}$ (25°C)¹³, $K_2 = 5.70 \cdot 10^{-2} \text{ atm}^{-1}$ (40°C)¹⁴. For the hydrogen bond energy $\epsilon_{OH} = 23305 \text{ J/mol}$ ¹⁵ the dimerization constant is in good agreement with literature data, whereas the trimerization constant is about three times as large as the literature value. An important and early study of organic associated vapours was made by Lambert, Rowlinson *et al.*¹⁶ Their values of association constants (K_2) are larger about one order of magnitude than our values.

4 STANDARD STATISTICAL CALCULATION OF DIMERIZATION CONSTANT OF METHANOL IN GAS PHASE

In this section we reject all approximations imposed by the lattice model and calculate for the sake of comparison the dimerization constant (K_p) of methanol gas in a standard statistical way,^{17,18,19} using the following relation

$$K_2 = \frac{1}{kT} \left(\frac{h^2}{\pi mkT} \right)^{3/2} \frac{z_{\text{int}}(A_2)}{[z_{\text{int}}(A_1)]^2}$$

where $z_{\text{int}}(A_2)$ and $z_{\text{int}}(A_1)$ are the internal partition function of methanol dimer and monomer, respectively, m is a mass of a single methanol molecule; k is the Boltzmann constant, h is the Planck constant, T is the absolute temperature. In a standard procedure the internal partition function $z_{\text{int}}(A_i)$ is given by

$$z_{\text{int}}(A_i) = z_{\text{rot}}(A_i)z_{\text{vib}}(A_i)z_{\text{el}}(A_i)$$

where $z_{\text{rot}}(A_i)$, $z_{\text{vib}}(A_i)$ and $z_{\text{el}}(A_i)$ are the contributions to $z_{\text{int}}(A_i)$ of rotational, vibrational and electronic degrees of freedom, respectively.

So

$$K_2 = \frac{1}{kT} \left(\frac{h^2}{\pi mkT} \right)^{3/2} \frac{z_{\text{rot}}(A_2)}{[z_{\text{rot}}(A_1)]^2} \frac{z_{\text{vib}}(A_2)}{[z_{\text{vib}}(A_1)]^2} \frac{z_{\text{el}}(A_2)}{[z_{\text{el}}(A_1)]^2} \quad (4)$$

The first step is to take the known molecular geometry of the methanol monomer and assume a molecular geometry for the dimer, (see the appendix for details).

In the dimer, besides the rotations of two methyl groups around their axes, there occurs an additional rotation of single molecule around the O---O line. In other words there are three degrees of freedom of internal rotation in the dimer and one in the monomer molecule. Neglecting the energy barriers for internal rotations, the rotational partition functions are

$$\begin{aligned} z_{\text{rot}}(A_1) &= \frac{1}{s_1 \Pi} \frac{1}{s_1 \pi} \left(\frac{8\pi^3 kT}{h^2} \right) I(A_1) \\ z_{\text{rot}}(A_2) &= \frac{1}{s_2 \Pi} \frac{1}{s_2 \pi} \left(\frac{8\pi^3 kT}{h^2} \right)^3 I(A_2) \end{aligned} \quad (5)$$

where s_1 and s_2 are the symmetry numbers ($s_1 = 3$, $s_2 = 9$) and $I(A_i)$ are the reduced moments of inertia.^{18,20} These reduced moments amount to

$$\begin{aligned} I(A_1) &= 1.1172 \cdot 10^{-78} \text{ (g} \cdot \text{cm}^2)^2 \\ I(A_2) &= 5.1145 \cdot 10^{-116} \text{ (g} \cdot \text{cm}^2)^3 \end{aligned}$$

The method of calculation of $I(A_i)$ is described in the appendix. So

$$\frac{z_{\text{rot}}(A_2)}{[z_{\text{rot}}(A_1)]^2} = \frac{165.04}{T} \quad (6)$$

There are five new vibrational degrees of freedom of the dimer, created by the formation of the hydrogen bond. Therefore the vibrational contribution to K_2 , in the harmonic oscillator approximation, is given by

$$\frac{z_{\text{vib}}(A_2)}{[z_{\text{vib}}(A_1)]^2} \simeq \prod_{i=1}^5 [1 - \exp(-\beta h\nu_i)]^{-1} \quad (7)$$

This equality is exact only when the frequencies of vibrations in the monomer do not change when two monomers form the dimer. Because frequencies in the monomer are rather high ($h\nu_i = 3680 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$) and changes $\Delta\nu_i$ are small (about few percents) Eq. (7) may be used. There are no literature data on five fundamental frequencies of the hydrogen bond in the gas methanol dimer. In this situation we selected the following five frequencies found in the

TABLE VI

Examples of Association constants K_2 methanol gas from the standard statistical calculation.

T[K]	$\epsilon_{\text{OH}}[\text{J/mol}]$					
	-12552	-16736	-20902	-23305	-25104	-29288
298.15	$8.65 \cdot 10^{-4}$	$4.68 \cdot 10^{-3}$	$2.53 \cdot 10^{-2}$	$6.62 \cdot 10^{-2}$	$1.37 \cdot 10^{-1}$	$7.40 \cdot 10^{-1}$
313.15	$6.64 \cdot 10^{-4}$	$3.31 \cdot 10^{-3}$	$1.65 \cdot 10^{-2}$	$4.13 \cdot 10^{-2}$	$8.24 \cdot 10^{-2}$	$4.11 \cdot 10^{-1}$
373.15	$2.89 \cdot 10^{-4}$	$1.11 \cdot 10^{-3}$	$4.29 \cdot 10^{-3}$	$9.25 \cdot 10^{-3}$	$1.65 \cdot 10^{-2}$	$6.37 \cdot 10^{-2}$
500	$1.02 \cdot 10^{-4}$	$2.80 \cdot 10^{-4}$	$7.66 \cdot 10^{-4}$	$1.36 \cdot 10^{-3}$	$2.10 \cdot 10^{-3}$	$5.73 \cdot 10^{-3}$
1000	$3.08 \cdot 10^{-5}$	$5.09 \cdot 10^{-5}$	$8.43 \cdot 10^{-5}$	$1.12 \cdot 10^{-4}$	$1.39 \cdot 10^{-4}$	$2.31 \cdot 10^{-4}$

low-temperature form of solid methanol as reported by Pellegrini *et al.*²¹ $h\nu_1 = 680 \text{ cm}^{-1}$, $h\nu_2 = 178 \text{ cm}^{-1}$, $h\nu_3 = 146 \text{ cm}^{-1}$, $h\nu_4 = 108 \text{ cm}^{-1}$, $h\nu_5 = 90 \text{ cm}^{-1}$.

The electronic contribution to K_2 has the form

$$\frac{z_{\text{el}}(A_2)}{[z_{\text{el}}(A_1)]^2} = \exp(-\beta\epsilon_{\text{OH}}) \quad (8)$$

where ϵ_{OH} is the hydrogen bond energy.

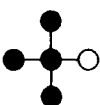
Now using Eqs. (4)–(8) we can calculate the dimerization constant K_p . Values of K_2 for several temperatures and several hydrogen bond energies are summarised in Table VI.

All K_2 values from the standard statistical method are larger than the values calculated with the aid of lattice model (Table V). No differences in order of magnitude appear for lower temperatures, for higher temperatures differences are larger, but all respective values are contained within one order of magnitude. In the lattice model we neglected completely the vibrational degrees of freedom and replaced the translational and the rotational contributions to K_2 with one term $G_2 = g_2 B$, whereas in the standard statistical method we assume a free internal rotation and describe vibrations by the harmonic oscillator approximation.

5 DISCUSSION

We have applied the lattice model to the calculation of association constants of model methanol molecules in the dilute solution of a nonpolar solvent (K_p^∞) and in the gas phase (K_p). In all considered models, except that of Sarolea, the successive linear association constants (K_p^∞) are equal or almost equal and if we neglect cyclic complexes the Mecke-Kempton model is obtained with all K_p^∞ ($K_p^\infty = K_x^\infty$) equal. The assumptions of Sarolea are discussed above in the text. Next it is necessary to take into account cyclic

structures (specially trimers and tetramers). Then $K_2/(K_3^{\text{lin}} + K_3^{\text{cy}}) = 0.045 \div 0.16$ and $K_2/K_3^{\text{lin}} = 1 \div 1.3$, depending on the assumed lattice model. For alcohol molecules with steric hinderances the Mecke-Kempton model is not obtained; the successive linear association constants progressively decrease ($K_2^\infty/K_3^\infty = 2.25$, $K_2^\infty/K_4^\infty = 6.0$ for the case of tert-

butanol  and simple square lattice).

In all considered lattice models of methanol solution a nonpolar solvent molecule is taken as a monomer occupying one lattice site and filling all available holes. Then any configuration is determined by the configuration of the solute molecules. Moreover, the shape and the size of alcohol molecule is very seriously distorted. We have tried to avoid this for a model without any solvent but with monomer holes (i.e., lattice gas). The dimerization constant of lattice methanol calculated in such multisite model which keeps the stereochemistry of CH_3OH relatively undistorted, and allows for an existence of cyclic trimers and tetramers, is in good agreement with semi-empirical data whereas the trimerization constant is about three times larger than literature value¹³ whose reliability is difficult to assess.

We also carried out a calculation of K_2 for the methanol gas by the standard statistical method,^{17,18,19} analysing the contributions to the dimerization constant of different degrees of freedom. There was a serious difficulty with the five new degrees of freedom of the methanol dimer, created by the formation of the hydrogen bond. There are no literature data on the fundamental frequencies of the hydrogen bond. The dimerization constant strongly depends on the adopted frequencies because these frequencies are low. We select the five fundamental frequencies from the frequencies for a low temperature form of solid methanol, published by Pellegrini *et al.*²¹ The calculated values of K_2 are larger than the results obtained within the lattice models, but differences do not exceed one order of magnitude. In the standard statistical method we use a high-temperature approximation to calculate the rotational partition functions and the harmonic oscillator approximation for the vibrational contribution to K_2 as can be seen from Eqs. (4)–(8). In lattice model calculation the vibrations of hydrogen bond were not taken into account, and the translational and the rotational contributions were determined together by one term $G_2 = B \cdot g_2$ (the number of configurations of dimer on a lattice). Here B is the number of lattice sites and corresponds to volume V (which appears in the translational partition function) and the combinatorial factor g_2 represents the internal rotation and the rotation of the whole molecule.

Finally all values of association constants will depend very strongly on the value of hydrogen bond energy (possibly solvated for a solution). This value must be known or assumed arbitrary.

APPENDIX

The molecular geometries of methanol monomer and dimer are shown in Figures 2 and 3. As can be seen from Figure 2 the geometry of methanol is

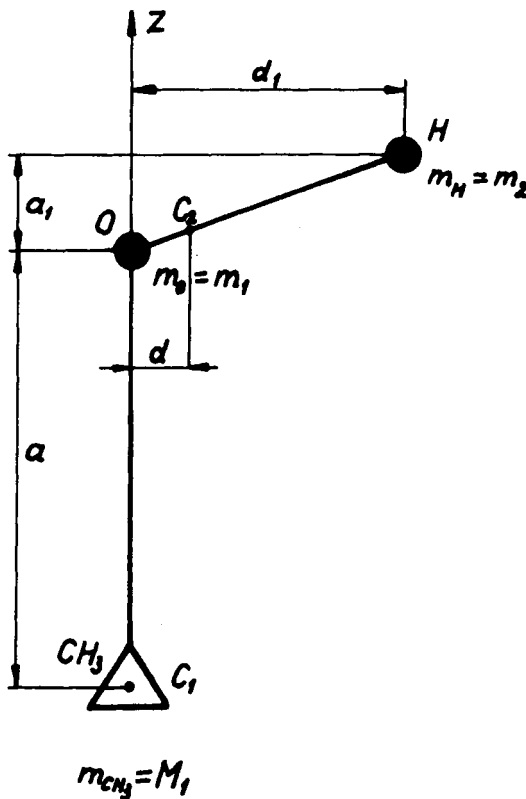


FIGURE 2 Methanol monomer; C₁ and C₂ points denote the mass centers of methyl and hydroxyl groups, respectively.

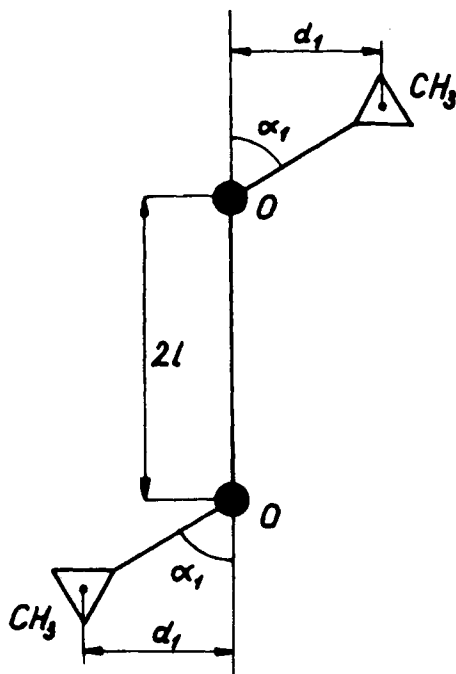


FIGURE 3 Methanol dimer; hydrogen atoms of hydroxyl groups, as not affecting much on the value of moment of inertia are neglected.

slightly simplified in putting the C—O bond symmetrically with regard to the CH₃ pyramid. Then the reduced moments of inertia $I(A_i)$ are given by

$$I(A_1) = \{F[\mu(a^2 + d^2) + \mu_1(a_1^2 + d_1^2) + E] \\ \times [\mu\mu_1(ad_1 - a_1d)^2 + (\mu d^2 + \mu_1 d_1^2)E]\}^{1/2}\dagger$$

where F , E are the main moments of inertia of methyl group; $F = I_{zz}$, $E = I_{xx} = I_{yy}$ and μ , μ_1 are the reduced masses defined as follows

$$\mu = \frac{M_1 M_2}{(M_1 + M_2)}, \quad \mu_1 = \frac{m_1 m_2}{(m_1 + m_2)}, \quad M_2 \equiv m_1 + m_2$$

$$I(A_2) = \frac{1}{2} \int_0^{2\pi} d\alpha [\det W(\alpha)]^{1/2} (9), \quad \det W(\alpha) = W_1(\alpha) W_2(\alpha)^*$$

$$W_1(\alpha) = \begin{vmatrix} A' & -J/2 & B' \\ -J & F & 2C' \\ B' & C' & G' \end{vmatrix}^*, \quad W_2(\alpha) = \begin{vmatrix} E' & -2J & K' \\ -J & F & D' \\ K' & 2D' & H' \end{vmatrix}^*$$

† These relations were derived by Mr A. Poniewierski

where

$$\begin{aligned}
 A' &= [A \sin^2(\alpha/2) + B \cos^2(\alpha/2) + G]/2 \\
 B' &= (D - K)\cos(\alpha/2) \\
 C' &= L \cos(\alpha/2) \\
 E' &= 2[A \cos^2(\alpha/2) + B \sin^2(\alpha/2) + G] \\
 G' &= 2[(B + E)\sin^2(\alpha/2) + H \cos^2(\alpha/2) + C] \\
 H' &= 2[(A + E)\cos^2(\alpha/2) + H \sin^2(\alpha/2) + C] \\
 K' &= 2(D + K)\sin(\alpha/2) \\
 A &= \mu d^2 \\
 B &= M_1 d^2 \\
 C &= m_1 l^2 + M_1 a^2 \\
 D &= M_1 a d \\
 G &= E \sin^2 \alpha_1 + F \cos^2 \alpha_1 \\
 H &= E \cos^2 \alpha_1 + F \sin^2 \alpha_1 \\
 K &= (\frac{1}{2})(F - E)\sin 2\alpha_1 \\
 J &= F \cos \alpha_1 \\
 L &= F \sin \alpha_1
 \end{aligned}$$

Similar expressions for reduced moments of inertia were obtained by Kassel²⁰ who evaluated I for nonrigid molecules. We calculated the integral (9) numerically, adopting the following values¹¹ of bond lengths and angles between bonds: $d_{\text{O-H}} = 0.953 \text{ \AA}$, $d_{\text{C-O}} = 1.423 \text{ \AA}$, $d_{\text{C-H}} = 1.092 \text{ \AA}$, $d_{\text{O...O}} = 2.67 \text{ \AA}$, $\angle \text{C-O-H} = 108.87^\circ$, $\angle \text{C-O...O} = 119.03^\circ$. The final values are $I(A_1) = 1.1172 \cdot 10^{-78} (\text{g} \cdot \text{cm}^2)^2$ and $I(A_2) = 5.1145 \cdot 10^{-116} (\text{g} \cdot \text{cm}^2)^3$.

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