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Transferable Intermolecular Potential Functions. Application to Liquid Methanol Including Internal Rotation[1]

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Abstract: Two transferable intermolecular potential functions for the methanol dimer have been used in Monte Carlo statistical mechanics simulations of liquid methanol at 25 °C. One function employs the three-site TIP model for a monomer, while the other retains the methyl hydrogens explicitly in a six-site model. The sampling with the latter potential included the internal rotation for the first time in a Monte Carlo calculation. It is found that the liquid's structure does not alter the dihedral angle distribution from the gas-phase result. Both functions show improved agreement with experimental thermodynamic and structural data in comparison to a previous simulation based on a potential function derived from quantum mechanical calculations. The success of the simple TIP model indicates that treating the methyl hydrogens implicitly is reasonable. Winding hydrogen bonded chains dominate the liquid's structure. Most monomers participate in one or two hydrogen bonds which are bent an average of 20°.

I. Introduction

For initiatiation of a program for the extensive theoretical study of organic chemistry in solution, computer simulations for a variety of polar solvents have been performed.[3-6] Future efforts will be directed towards dilute solutions of organic ions and neutral substrates as well as the characterization of potential surfaces for simple reactions in liquids. A critical component in the research is the need for simple, transferable intermolecular potential functions (TIPS) describing the interactions between molecules in the fluids. The potential functions for the initial studies were derived from quantum mechanical calculations on appropriate dimers.[3-6] However, the functions were not transferable and the need to properly account for dispersion effects has become increasingly apparent as the size of the monomers grows. Unfortunately, post-Hartree–Fock treatments are then necessitated, but they are computationally practical only for small dimers.

As an alternative, TIPS have been derived empirically in the preceding paper for water, alcohols, and ethers.[7] Parameters were adjusted to be consistent with earlier work on liquid hydrocarbons and to yield reasonable results for liquid water and trends for series of dimers. The viability of this approach and the quality of the TIPS can only be tested by employing them in additional liquid simulations. Consequently, the results of a Monte Carlo simulation of liquid methanol using the TIPS model are reported here. A Monte Carlo calculation with another potential function, MHL, which represents the methyl hydrogens explicitly has also been performed for methanol. The sampling in the latter case included the internal rotation of the methyl group.

The structural and thermodynamic results from the TIP- and MHL-based simulations show significant improvement over the original study of methanol with the quantum mechanical potential function.[6] Furthermore, the similarity of the TIP and MHL results indicates that the simplification of treating the hydrogens of alkyl groups implicitly is acceptable. It is also found that the liquid's structure does not alter the dihedral angle distribution for the methyl rotation from the ideal gas result. Overall, the viability of the TIP approach is given strong support.

II. The Intermolecular Potential Functions

Two intermolecular potential functions for the methanol dimer have been utilized here. The first is the TIP function which has been thoroughly discussed in the preceding paper.[7] The methanol monomer is represented by three interaction sites, the methyl group centered on carbon and the oxygen and hydroxyl hydrogen atoms. Intermolecular interactions involve Coulomb and Lennard–Jones terms between all pairs of sites in the different monomers according to eq 1.

Table I. Results for Methanol Dimers from the TIP and MHL Functions[a]

	r_{OO}	θ	$-\Delta E$
	linear		
TIP	2.79	27	5.68
MHL	2.80	29	5.29
6-31G*[b]	2.95	48	5.66
	cyclic		
TIP	2.80	42	4.25
MHL	2.87	46	3.50

[a] Distances in Å, angles in deg, dimerization energies in kcal/mol. Geometric parameters are defined in ref 7 and 9. [b] Reference 11.

$$\Delta E = \sum_{a}^{\text{in } A} \sum_{b}^{\text{in } B} \left(\frac{q_a q_b e^2}{r_{ab}} + \frac{A_a A_b}{r_{ab}^{12}} - \frac{C_a C_b}{r_{ab}^{6}} \right) \tag{1}$$

For assessment of the effect of treating the methyl hydrogens explicitly, a six-site model for methanol has also been developed that employs an interaction site on every atom. The function is a modified version of the Hagler–Lifson potential functions for carboxylic acids and amides, so it will be referred to as the MHL potential.[8] The form is the same as eq 1 except an r^{-9} term replaces the r^{-12} term for the short-range repulsions. For methanol, the parameters for the r^{-9} and r^{-6} terms were adopted from those for alkyl C, H_C, and O_H in the carboxylic acids.[8] The charge for H_C (+0.11 e)[8] was also assumed to be transferable. The charges for O and H_O in methanol were optimized to yield reasonable results for the geometries and energies of linear and cyclic methanol dimers in the gas phase.[9] The resultant values were −0.59 e for O and +0.41 e for H_O. This leads to −0.15 e for q_C to preserve neutrality. The experimental geometry for a monomer has been used throughout this study with the MHL potential.[10] Specifically, the OH, CH, and CO bond lengths are 0.9451, 1.0936, and 1.4246 Å, and the COH and HCO angles are 108.533 and 110.297°.[10] These parameters are consistent with the standard values employed with the TIP function.[7] The reason for the slight differences is historical; the MHL potential was actually develped and used in the liquid simulation several months prior to the advent of the TIP model.

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[1] Quantum and Statistical Mechanical Studies of Liquids. 11.

[2] Camille and Henry Dreyfus Foundation Teacher-Scholar, 1978–1983; Alfred P. Sloan Foundation Fellow, 1979–1981.

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[7] Jorgensen, W. L., preceding paper in this issue.

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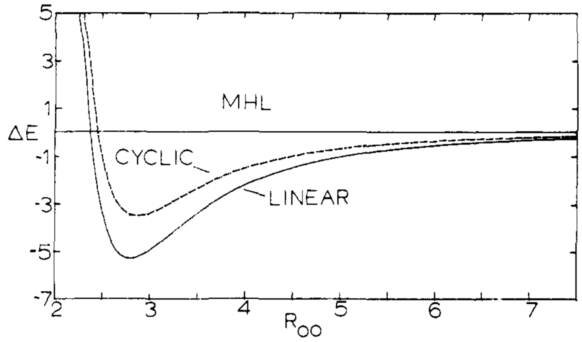


Figure 1. Variation of dimerization energies (kcal/mol) with OO separation (Å) for methanol dimers from the MHL potential.

The dipole moments from the TIP and MHL models for methanol are similar, 2.21 and 2.16 D, respectively. Predictions for linear and cyclic methanol dimers are compared in Table I. The ab initio results of Tse et al. with the 6-31G* basis set are also shown for the linear dimer.[11] The MHL optimizations assumed staggered monomers. The TIP and MHL findings are close, though the dimerization energies are somewhat lower with TIP. As discussed at length previously,[7,9] the experimental dimerization energies vary substantially, but a value of 5–6 kcal/mol is a good estimate.

The shorter OO distance for the linear dimer from the potential functions than from the 6-31G* data is consistent with the shorter OO distance in the water dimer needed to properly position the first peak in the OO radial distribution function (g_{OO}) for liquid water.[7] Since the first peak for alcohols falls experimentally between 2.7 and 2.9 Å,[12,13] the prediction of 2.8 Å for the dimers is desirable.

The dependence of the dimerization energies for the linear and cyclic dimers on OO separation is displayed in Figure 1 for the MHL potential. The curve for the linear dimer from the TIP function, shown in Figure 3 of the preceding paper,[7] virtually coincides with the MHL results except in the immediate vicinity of the minimum. These and other tests have established that the TIP and MHL potential surfaces for the methanol dimer are very similar, although the latter includes the methyl hydrogens explicitly.

III. Monte Carlo Simulations

A. Procedure. Monte Carlo simulations were executed for cubic samples of 128 monomers at 25 °C, using the experimental density 0.78664 g/cm^3.[14] Therefore, an edge of the cube is 20.534 Å long. Most details are the same as in the earlier study.[6] Periodic boundary conditions, Metropolis sampling, and a spherical cutoff at an OO separation of 9 Å were employed. The energy of a configuration was obtained from the pairwise sum of the dimerization energies plus the internal rotational energy when appropriate. Various aspects of such calculations including system size and the neglect of threebody interactions have been discussed previously.[3-6]

The results of three simulations will receive attention below. Besides the one based on the TIP function, the MHL potential was used in a simulation with the internal rotation included and with the monomers held rigid in the staggered conformation ($\phi = 60°$). The latter two simulations will be referred to as MHL and MHLR, respectively. For the MHL run, a threefold internal rotational barrier was included for each monomer with the experimental height (V_0) of 1.07 kcal/mol[10] such that $V(\phi) = V_0(1 + \cos 3\phi)/2$.

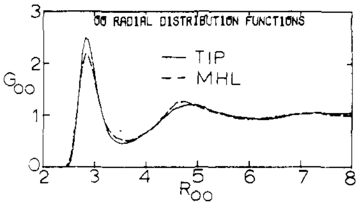


Figure 2. OO radial distribution functions for liquid methanol at 25 °C from the Monte Carlo simulations. Interatomic distances are in Å throughout.

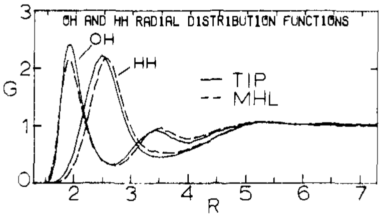


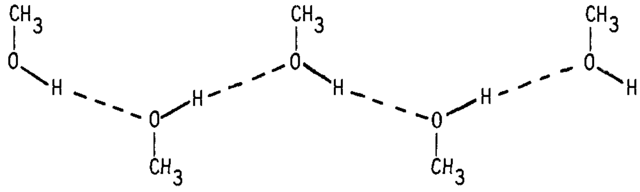
Figure 3. OH_O and H_OH_O radial distribution functions for liquid methanol at 25 °C.

A move to generate a new configuration involved randomly picking a monomer, translating it in all three Cartesian directions, rotating it about one randomly chosen axis, and, for the MHL simulation, performing the internal rotation. Acceptance rates of 40–50% for new configurations were obtained by using ranges of ca. ±0.16 Å for the translations, ±16° for the complete molecular rotation, and ±12° for the internal rotation. Initial configurations were based on earlier runs. To our knowledge, the MHL simulation was the first Monte Carlo calculation to include an internal rotation. A potential problem is that ergodic difficulties could be encountered if the rotational barrier is too high; i.e., the configuration space would not be fully sampled. In order for the sampling efficiency to be monitored, the starting distribution of dihedral angles in the MHL run was deliberately taken as non-Boltzmann; all monomers were initially eclipsed ($\phi = 0°$). For each simulation, energetic equilibrium was well established after 250–300K attempted moves. Averaging for results took place over an additional 400K configurations in each case.

The Monte Carlo calculations were executed on the CDC/6600 system at Purdue and on the CDC/7600 at the Lawrence Berkeley Laboratory.

B. Radial Distribution Functions. The average density of y atoms at a distance r from an atom of type x in a liquid is given by $\rho_{xy}(r) = \rho_y{}^\circ g_{xy}(r)$, where $\rho_y{}^\circ$ is the bulk density of y atoms (N_y/V) and $g_{xy}(r)$ is the xy radial distribution function (RDF). Thus, g_{xy} represents fluctuations in the local density due to structure in the liquid.

The OO, OH_O, and H_OH_O RDF's from the TIP and MHL simulations are compared in Figures 2 and 3. The peaks can be assigned with the aid of a simple chain model reminiscent of the solid[15] as shown in I. It is emphasized that this is a severe oversimplification for the liquid's structure.[6]



I

There are many points to note. (1) The RDF's from the TIP and MHL simulations are nearly identical. The first peaks are a little higher with the TIP function which is consistent with the slightly deeper hydrogen bonding well. All the RDF's from the MHL and MHLR runs are identical within the statistical limits of the calculations except for some minor difference for the RDF's

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(12) (a) Harvey, G. G. *J. Chem. Phys.* **1938**, *6*, 111. (b) Wertz, D. L.; Kruh, R. K. *Ibid.* **1967**, *47*, 388. (c) Harvey, G. G. *Ibid.* **1939**, *7*, 878.

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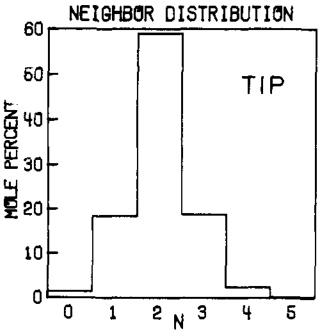

Figure 4. Distribution of neighbors for monomers in liquid methanol within the range of the first peak in the OO radial distribution function.

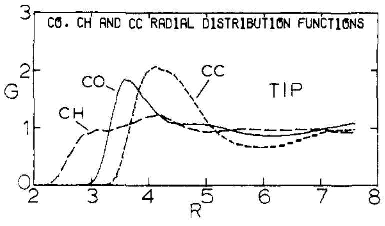

Figure 5. CO, CH_O, and CC radial distribution functions for liquid methanol at 25 °C.

involving the methyl carbon and hydrogens. Consequently, the RDF's from the MHLR run will not be displayed.

(2) Peaks due to the first, second, and third nearest neighbors are apparent in both g_{OO}'s. The first peak integrates to 2.0 neighbors in both cases consistent with I. As usual, configurations were saved every 2000 attempted moves during the runs. The distributions of neighbors in the first peaks of g_{OO}, i.e., within an OO separation of ca. 3.6 Å, were analyzed. The results for the TIP simulation are shown in Figure 4 and confirm the inaccuracy of I. Only about 60% of the monomers have exactly two nearest neighbors with the remainder roughly split between one and three neighbors. This is consistent with branched chains and/or rings. The structure beyond the first peak in g_{OO} is encouraging in view of the flatness of g_{OO} in this region for the TIP simulation of water.[7]

(3) The X-ray analysis of liquid methanol is not as refined as for water.[12] However, Harvey[12a] and Wertz and Kruh[12b] both assign an OO peak at 2.7 Å with an area of 2. The calculated peaks in Figure 2 both occur at 2.81 Å. This is certainly within the limits of the accuracy of the experimental assignments. The agreement of the experimental results actually provides some cause for concern since Harvey did not correct for background and ran the experiments at −75 °C, while the measurements of Wertz and Kruh were at 25 °C. Hopefully, additional experiments will be undertaken.

(4) The heights of the first peaks in g_{OO}, g_{OH}, and g_{HH} are substantially reduced from their values of 3–4 in the simulation with the quantum mechanical potential.[6] This is undoubtedly desirable because all evidence indicates that the peaks are too high from the quantum mechanical potentials for water, hydrogen fluoride, and methanol due to the overly narrow hydrogen bonding wells predicted by minimal basis set calculations.[3,4,6,9]

(5) The first peaks in g_{OH} are for the hydrogen bonds and integrate to 0.90–0.95 which implies an average of 1.8–1.9 hydrogen bonds per monomer. The first peak in g_{HH} integrates to ca. 2.5, whereas 2 would be expected from I.

The CO, CH_O, and CC RDF's from the TIP simulation are shown in Figure 5. The MHL results are nearly identical. The peaks for g_{CO} and g_{CC} occur at 3.6 and 4.1 Å. Wertz and Kruh assign CO and CC peaks in $\Gamma(r) = 4\pi r^2 \rho g(r)$ at 3.8 and 4.4 Å. From the calculated RDF's, maxima in Γ are predicted at 3.7 and 4.45 Å. The broad band in g_{CC} could certainly be decomposed into two peaks due to inter- and intrachain contributions. The results from the quantum mechanical potential are qualitatively similar. Since they have been analyzed thoroughly elsewhere,[6] the discussion will not be repeated here. This also applies to the description of the general structural features of liquid methanol which remains unchanged.[6] Along these lines, stereoplots of configurations from the present simulations are similar to those previously reported and clearly reveal that polymeric chains dominate the liquid's structure.

Table II. Thermodynamic Results for Liquid Methanol at 25 °C[a]

	TIP	MHL	MHLR	exptl
$-E_i^{inter}$	7.16	7.43	7.21	
E_i^{rot}		0.32		$(0.32)^b$
$-E_i$	7.16	7.11	7.21	
C_V	16.3^c	20.1^c	14.3^c	15.9^d
$\Delta H_V°$	7.76	8.02	7.80	9.07^d

[a] Energies in kcal/mol; heat capacities in cal/(mol deg). [b] Ideal gas value. [c] Includes ideal gas term. [d] See ref 6 and 14.

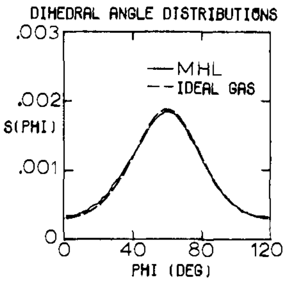

Figure 6. Dihedral angle distributions for the monomers in liquid methanol at 25 °C from the Monte Carlo simulation and for the ideal gas. The units for the ordinate are mole percent per degree.

C. Thermodynamics and Internal Rotation. The thermodynamic results from the simultations are summarized in Table II along with experimental data for the heat capacity, C_V, and the enthalpy of vaporization for the liquid going to the ideal gas, $\Delta H_V°$. E_i is the internal potential energy for the liquid which is made up of an intermolecular term, E_i^{inter}, and the energy due to the intramolecular rotation, E_i^{rot}. E_i^{inter} includes a cutoff correction (−0.23 kcal/mol).[7] The theoretical C_V's consist of the computed term for the variance of the intermolecular potential energy and a correction for the unimolecular contribution approximated by the heat capacity of the ideal gas, $C_V°$ (8.5 kcal/mol at 25 °C). Standard deviations (σ) for the computed E_i, E_i^{rot}, and C_V^i were obtained from control functions and are 0.03 kcal/mol, 0.005 kcal/mol, and 2.0 cal/(mol deg), respectively, for the MHL simulation. Similar values apply to the TIP and MHLR calculations. $\Delta H_V°$ is computed from eq 2 and 3.

$$\Delta H_V° = \Delta E_V° + P(V°(g) - V(l)) \quad (2)$$

$$\Delta E_V° \approx -E_i^{inter} + E_i^{rot}(\text{ideal gas}) - E_i^{rot}(l) \quad (3)$$

The computed $\Delta H_V°$'s all underestimate the experimental value by ca. 15% which is reasonable owing to the neglect of three-body effects. They show marked improvement over the $\Delta H_V°$ of 6.7 kcal/mol from the quantum mechanically based potential.[6] The computed C_V's appear to be in accord with experiment when the standard deviations and slow convergence of the C_V's are considered.[16]

The energy of internal rotation for the ideal gas was calculated from a Boltzmann distribution and agrees exactly with the computed value for the liquid in the MHL simulation. Furthermore, the distribution of populations for the dihedral angle, $S(\phi)$, was found to be the same for the liquid and the ideal gas, as illustrated in Figure 6. Thus, the liquid's structure does not affect the dihedral angle distribution. This is sensible electrostatically since the dipole moment is invariant to ϕ in the potential, and packing effects for the methyl hydrogens at the liquid density should not be significant. No evidence of sampling problems was evident for this low barrier; E_i^{rot} was well converged, and $S(\phi)$ was nearly threefold symmetric over the full 360° range.

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(16) Mezei, M.; Swaminathan, S.; Beveridge, D. L. *J. Chem. Phys.* **1979**, *71*, 3366.

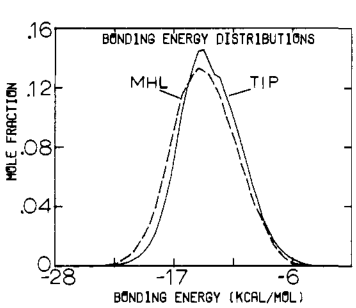

Figure 7. Distributions of intermolecular bonding energies for monomers in liquid methanol.

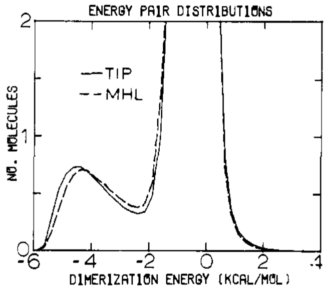

Figure 8. Distributions of dimerization energies for a monomer in liquid methanol. The units for the ordinate are molecules/kcal mol^{-1}.

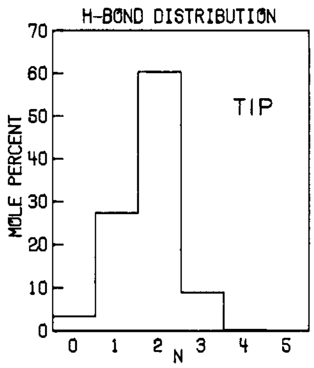

Figure 9. Distribution of coordination numbers for hydrogen-bonded monomers from the simulation with the TIP function. A hydrogen bond is defined by a dimerization energy below −2.25 kcal/mol.

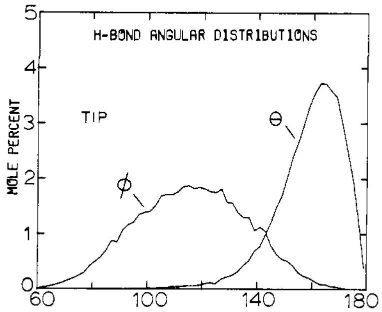

Figure 10. Distributions for the hydrogen-bonding angles between monomers with dimerization energies below −2.25 kcal/mol. The units for the ordinate are mole percent per degree. θ is the O–H···O angle, and ϕ is the H···O–H angle. Results are from the TIP simulation.

Systematic analysis is required to assess the limits of this approach to studying internal rotation in liquids. Interesting work in this area has been performed by Chandler and co-workers.[17] They predict significant solvent effects on the conformational preferences of butane. The nature of the barrier in this case is quite different than for methanol since it is higher and contains two minima. In the accompanying study of ethanol, the condensed phase again does not affect the dihedral angle distribution for rotation about the CO bond.[18]

One additional item worth noting in Table II is that the intermolecular energy, E_i^{inter}, is lowered by 0.2 kcal/mol when the methyl rotation is permitted. However, as noted above, the effect on the RDF's is slight.

The distributions of total bonding energies and dimerization energies for monomers in the liquid are displayed in Figures 7 and 8. The monomers experience an energetic continuum of environments; some are bound by as little as 5 kcal/mol and some by as much as 23 kcal/mol. There is no reason a priori for the bonding energy curves to be symmetric. In fact, they are slightly skewed toward lower energy, though they remain unimodal. The shapes are consistent with the symmetry of the neighbor distribution in Figure 4. In contrast, the bonding energy distribution from the quantum mechanical potential was bimodal.[6] The coordination number from the first peak in g_{OO} was 2.6 in this case which significantly shifted the neighbor distribution to higher coordination numbers with a consequent loss of symmetry. Thus, it appears that the bimodal distribution was an artifact of the exaggerated first peak in g_{OO} and ultimately of the narrowness of the hydrogen bonding well from the quantum mechanical potential.[6]

The energy pair distributions have the usual shape with the peak at low energy due to the hydrogen-bonded neighbors. The minimum occurs at −2.25 kcal/mol and may be associated with an energetic limit for hydrogen bonding. Integration to this point yields average numbers of hydrogen bonds per monomer of 1.73 for the MHL simulation and 1.76 for TIP. This is consistent with the expectation from the integrals of the first peaks in g_{OH}. The spike near 0 kcal/mol is caused by the reference monomer's interactions with the many distant molecules in the liquid. In comparing the TIP results for water,[7] methanol, and ethanol,[18] a gradual shift of the spike toward lower energy is observed with increasing size of the monomers. This is attributable to the concomitant increasing importance of dispersion interactions.

D. Hydrogen-Bonding Analysis. Once the hydrogen-bonding limit has been set from the energy pair distribution, the saved configurations can be analyzed to quantify some features of the hydrogen bonding in the liquid. The distribution of hydrogen bond numbers is shown in Figure 9 from the TIP run. The percentages of monomers in 0–4 hydrogen bonds are 3, 27, 60, 9, and 0%. The MHL and MHLR results are nearly identical with the percentages 5, 32, 52, 11, and 0. As before, the monomers in 0–3 hydrogen bonds are assigned as free monomers, chain ends, interior to chains or rings, and Y junctions in chains.[6] All these species are apparent in stereo plots of the configurations. Winding chains are the dominant multimers; some rings, particularly four-membered, are apparent though they are relatively rare.[6] Since the ratio of monomers in one or two hydrogen bonds is 1:2 or 3:5, a rough estimate of the *average* chain length is 5–6 monomers. There is much infrared data on methanol and ethanol which supports the presence of hydrogen-bonded polymer and a variety of multimers.[19] Luck has estimated the fraction of "free" OH groups as ca. 3% which implies 6% chain ends assuming only head-to-tail chains in the liquid at 25 °C.[19a,d] The discrepancy with the higher calculated values is probably due to differences in the IR and theoretical definitions of being hydrogen bonded. Clearly, agreement could be obtained by invoking a more lenient energetic criterion in the computations. That the discrepancy is artificial is also suggested by the concurrence of the X-ray, IR, and the-

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(17) Pratt, L. R.; Hsu, C. S.; Chandler, D. *J. Chem. Phys.* **1978**, *68*, 4202. Hsu, C. S.; Pratt, L. R.; Chandler, D. *Ibid.* **1978**, *68*, 4213. Rebertus, D. W.; Berne, B. J.; Chandler, D. *Ibid.* **1979**, *70*, 3395.

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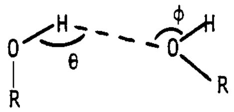
oretical results for the average number of nearest neighbors.[21]

Figure 10 shows the distributions for the hydrogen bond angles, θ and ϕ, illustrated in II. The potential functions prefer θ and ϕ values of roughly 180 and 110° for the linear dimer in the gas phase at 0 K. The MHL results for the distributions are virtually identical with the TIP curves and reveal a broad variety of angular combinations for hydrogen bonds. As discovered previously for the other hydrogen bonded liquids,[3–7] the average hydrogen bond is bent about 20° in liquid methanol.



It is important to emphasize that in the liquids there is a continuous spectrum of hydrogen bond strengths and geometries as illustrated in Figures 8 and 10. The *average* hydrogen bond energy in liquid methanol is predicted here to be ca. 4.5 kcal/mol which translates to an enthalpy of ca. 3.3 kcal/mol.[6] Experimental measurements at ambient temperature refer to these average values and are not directly related to the results of quantum mechanical calculations for the absolute minimum on the potential surface for the dimer at 0 K. Thus, apparent discrepancies of 1–2 kcal/mol between theoretical and experimental results may be accounted for in this manner.[6,20]

IV. Conclusion

A number of important findings have emerged in this study. The similarity of the MHL and TIP results and their accord with the available experimental thermodynamic and structural data for liquid methanol are strong support for the viability of the TIP model. The results also indicate that it is unnecessary to explicitly include the methyl hydrogens to obtain a reasonable description of the liquid. In addition, this work establishes that sampling in Monte Carlo calculations can include internal rotations; however, further study is needed to define the limits of the procedure. The liquid's structure was not found to affect the distribution of dihedral angles for rotation of the methyl group in the methanol monomers. The previous description of the qualitative features of the structure of liquid methanol was confirmed.[6] The liquid primarily consists of hydrogen-bonded chains of various lengths. Most monomers are in one or two hydrogen bonds, however, some monomers participate in three hydrogen bonds corresponding to branch points in the chains. The hydrogen bonds are flexible and have smooth distributions of strengths and distortions.

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(21) **Note Added in Proof**: In the review by Franks and Ives,[22] the authors state that the polymeric chains in liquid alcohols do **not** "exceed a complexity, *n*, of 5–7 molecules". However, in going over the original literature,[23] it appears that this claim was based on data for dilute solutions and not the pure liquids.

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Simulation of Liquid Ethanol Including Internal Rotation[1]

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Abstract: A Monte Carlo statistical mechanics simulation of liquid ethanol at 25 °C has been performed by using the TIP model to describe the intermolecular interactions. Detailed structural and thermodynamic information has been obtained and compares favorably with experimental results including X-ray and infrared data. The internal rotation about the CO bond in the monomers was included in the calculations. The liquid's structure was not found to alter significantly the distribution for the dihedral angle from the ideal gas result. Winding hydrogen-bonded chains are ubiquitous in the liquid, and some branching of the chains is evident. Smaller oligomers are also present, though the occurrence of cyclic multimers is relatively uncommon. The monomers in the liquid experience an energetic continuum of environments covering a 20-kcal/mol range. Furthermore, the hydrogen bonds are distributed in both energy and geometry with the average hydrogen bond bent 15–20° from linear. The overall success of the simulation emphasizes the value and utility of the TIP based approach to modeling fluids.

I. Introduction

Interest in ethanol has been flourishing due to its potential as a major fuel and raw material for the chemical industry.[3] Ethanol's importance as an organic solvent also makes it a key target for our theroetical studies of organic chemistry in solution. Progress cannot be made unless fluids with complex polar and nonpolar interactions can be treated. Consequently, a Monte Carlo statistical mechanics simulation of liquid ethanol at 25 °C has been carried out. This was facilitated by the recent development of transferable intermolecular potential functions (TIPS) for water, alcohols, and ethers.[4] The calculated structural and thermody-

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