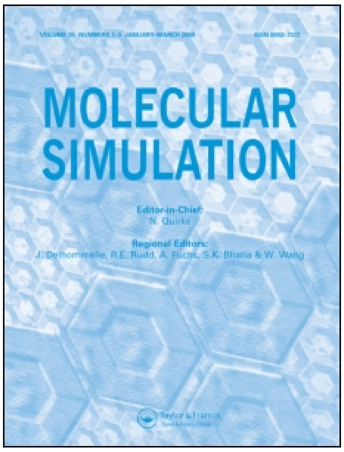

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MONTE CARLO STUDY OF THE SELF-ASSOCIATION OF METHANOL IN BENZENE

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Monte Carlo (MC) calculations have been carried out for four benzene–methanol solutions within conventional NVT ensemble by the Metropolis scheme. New potential functions have been prepared for benzene–benzene and benzene–methanol interactions. They are based on extensive LCAO SCF molecular orbital calculations with the Møller-Presset perturbation method and STO-3G basis set. For methanol–methanol interactions, the potential function proposed by Jorgensen is adopted. The mole fractions of methanol in the four benzene–methanol solutions studied are 0.05, 0.10, 0.25 and 0.5, respectively. The MC results clearly show the self-association of methanol, the degree of which increases with increasing the methanol content. It is also found that the shape of self-associating complex of methanol molecules changes from spherical in lower methanol content to flexible chain-like in concentrated solutions. The fraction of methanol molecules which exist as monomer is estimated for each solution and proved to be consistent generally with spectroscopic informations.

KEY WORDS: Monte Carlo, self-association, methanol, benzene.

INTRODUCTION

Alcohol-hydrocarbon mixtures are typical non-aqueous associated solutions in which one of the components, alcholol, is self-associated to varying degrees. Thus, because of incomplete mixing of one component, such solutions exhibit large positive deviations from the ideal solution law [1]. They are sometimes larger than those observed for aqueous solutions of alcohols. Results of such deviations are for example a complex behavior of activity coefficient as a function of composition and the presence of negative azeotropes. In addition to this thermodynamic evidence, there are also available spectroscopic data by which the presence of associated species is more clearly shown [2]. These facts suggest that alcohol-hydrocarbon mixtures are one of the most interesting solution systems be studied at the molecular level.

In spite of widespread application of the computer simulation technique in solution chemistry, there seem to be no extensive molecular simulation studies on alcohol-nonpolar molecule systems. In the present study, we have attempted to examine the state of self-association of methanol diluted in benzene at room temperature. For this purpose, we first determine benzene–benzene and benzene–methanol pair potential functions based on molecular orbital calculations and then, by using these potential functions together with the methanol dimer potential prepared by Jorgensen [3], we

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carry out NVT ensemble Monte Carlo calculations for benzene-rich regions of benzene–methanol mixtures. Based on the results obtained, we discuss the association state of methanol molecules which might change with increasing concentration of methanol.

POTENTIAL FUNCTIONS

Of three kinds of potential functions used in simulation in the whole composition ranges, benzene–benzene and benzene–methanol pair potential functions have been prepared based on the molecular orbital (MO) calculations for each kind of supermolecule. Actually, a benzene dimer potential function is available [4]. But we prepared a new one for consistency with our benzene–methanol potential. Since the interactions for those molecular pairs are not so large, we have to evaluate the dispersion force between two molecules. Thus we used the second-order perturbation method MP2 due to Møller and Presset (MP2) with the STO-3G minimal basis set.

The MO results thus obtained are used to determine the coefficients in the following equations for each pair potential with molecular model given in Figure 1.

Benzene–Benzene

$$V = \sum_{i,j} \left\{ \frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^4} + \frac{B_{ij}}{r_{ij}^6} + \frac{C_{ij}}{r_{ij}^9} + \frac{D_{ij}}{r_{ij}^{12}} \right\} \tag{1}$$

Benzene–Methanol

$$V = \sum_{i,j} \left\{ \frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^3} + \frac{B_{ij}}{r_{ij}^6} + \frac{C_{ij}}{r_{ij}^{12}} \right\} \tag{2}$$

Here, i and j are centers of interaction (atom, atomic group or dummy charge) in each molecule, Q_{ij}, A_{ij}, B_{ij}, C_{ij} and D_{ij} are the coefficients to be optimized, and r_{ij} is the

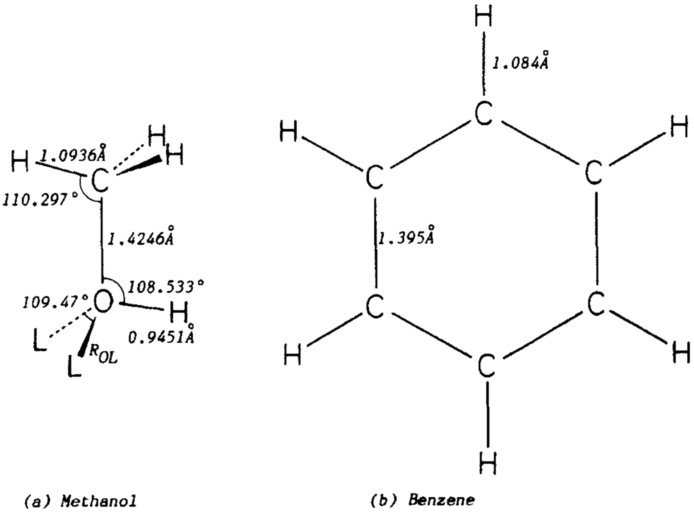


Figure 1 Model of methanol and benzene. L:dummy charges for lone pair electrons.

Table 1 Number of random configuration and standard deviations

system	*sample*		*fitted data (< 10 KJ/mol)*	
	range (A)	*total no.*	*using no.*	*σ (KJ/mol)*
Benzene–Benzene	1.5 ~ 8.5	236	132	0.457
Benzene–Methanol	1.5 ~ 6.5	409	72	0.870

Table 2 Parameters of Benzene–Benzene potential function.

i,j	Q_{ij}	A_{ij}	B_{ij}	C_{ij}	D_{ij}
C–C	5.187414726	−54.73953862	−360.7534957	39465.61921	629341.8969
C–H	−5.187414726	38.07406619	−296.1977447	3341.850711	58150.92010
H–H	5.187414726	−27.42202315	21.27821610	1551.193855	5673.018796

distance between *i* and *j*. Totally, 132 and 72 MO data for benzene–benzene and benzene–methanol pairs, respectively, each corresponds to different configuration of dimer, have been used for the optimization of the coeficients by a direct search method. Standard deviations from the original MO values and the optimized coefficients in Equations (1) and (2) are given in Tables 1, 2 and 3, respectively. Satisfactory results of optimization can also be seen from Figure 2 where calculated energy values from Equation (1) and (2) are plotted against original MO values for each configuration. For methanol–methanol interactions, the pair potential proposed by Jorgensen [3] is used.

In order to obtain an overview of the present potential functions, isoenergy contour maps have been prepared based on the above equations as in Figure 3. The benzene molecule is placed at the center of the map and contour lines are shown only on the two planes either parallel or perpendicular to the plate of benzene molecule. The potential energy minima for benzene–benzene and benzene–methanol are found to be −1.1 and −3.4 kJ/mol, respectively. This is to be compared with a large negative value of −30.5 kJ/mol for the minimum in methanol–methanol interactions [3].

MONTE CARLO CALCULATIONS

Using the three potential functions explained in the above section, we have carried out Monte Carlo calculations for benzene–methanol solutions at ordinary pressure. Emphasis is placed on the benzene-rich regions of the solution.

Table 3 Parameters of Benzene-Methanol potential function.

i,j	Q_{ij}	A_{ij}	B_{ij}	C_{ij}
C–O		−43.60271814	−462.7187128	805064.1943
−H	−11.33126567	−4.027674960	−121.4134665	143924.1954
−Me	−19.24726788	44.44454809	−487.6271583	3585509.998
−L	15.28926678			
H–O		37.13968639	−193.9220406	11869.23789
−H	11.33126567	−6.176262945	174.6562629	16267.79212
−Me	19.24726788	−27.77757844	−391.7009628	573438.6380
−L	−15.28926678			
		$R_{OL} = 0.8317286378$		

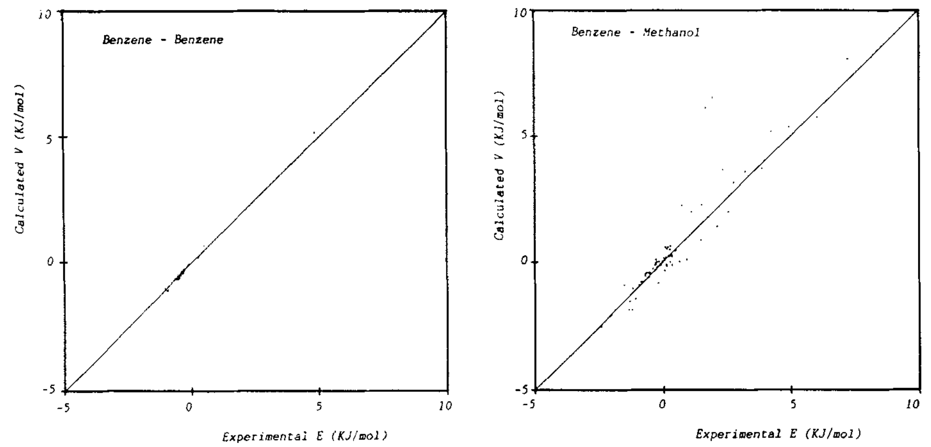


Figure 2 Reproducibility of MO data by Eqs. (1) and (2) with optimized parameters. V: calculated by Eqs. (1) and (2). E:MO values.

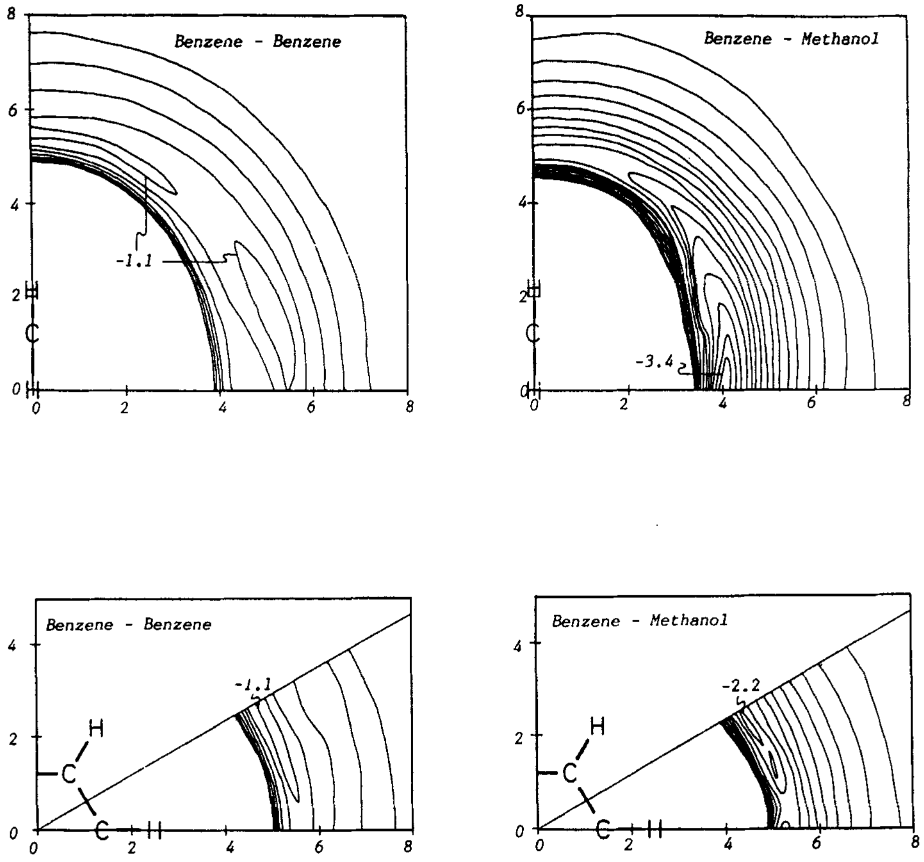
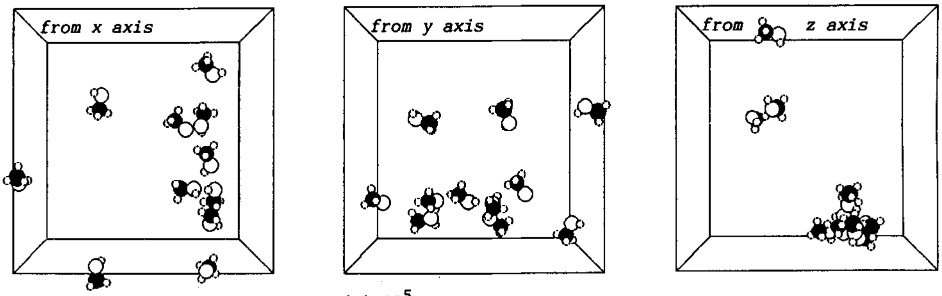
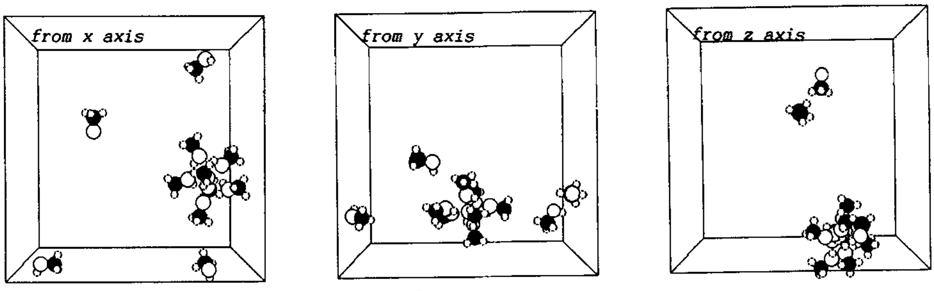


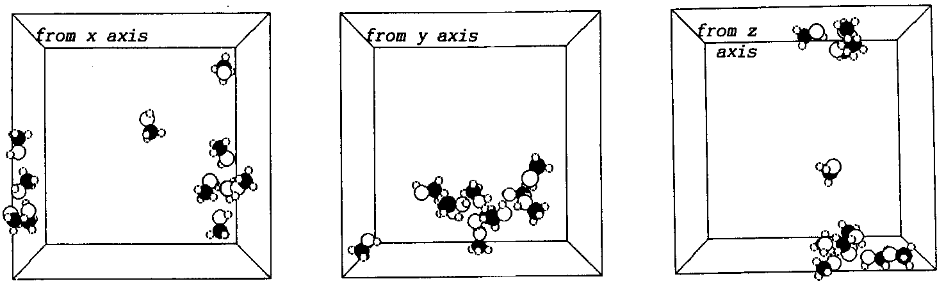
Figure 3 Isoenergy contour maps of benzene-benzene and benzene-methanol potentials. Upper: perpendicular to the benzene plate. Lower: on the benzene plate. Numbers in the figure indicate the potential well depth in kJ/mol.



(a) 10^5th step



(b) $8x10^5$th step



(c) $1.6x10^6$th step

Figure 4 Configuration of methanol molecules in 10 mol% methanol solution at three time steps. Black, large white and small white circles show carbon, oxygen and hydrogen atoms in methanol molecule, respectively.

The present Monte Carlo calculations have been done within an NTV ensemble using the conventional Metropolis scheme [5]. The total number of molecule N is always 108, the temperature of the solution is 298.15 K and the volume of the solution is determined from the experimental data of density [6]. We have performed four MC runs where the mole fractions of methanol are 0.05, 0.10, 0.25 and 0.50, respectively.

The initial configuration of each solution was a uniform distribution of methanol molecules on a cubic lattice. The periodic boundary condition is always applied. Then each Monte Carlo run was extended until the potential energy of the system decreased and exhibited stationary fluctuation. The total number of the MC steps (here one step means one accept/reject trial) of each run was between 1,600,000 and 2,600,000, and the final 500,000 to 1,000,000 configurations for each solution were used for the analysis of the results.

RESULTS AND DISCUSSION

Self-Association Process

There are many thermodynamic and spectroscopic evidences that alcohols and other associated liquids show a strong tendency to self-associate in nonpolar solvents. This tendency can be clearly shown from the results of the present MC calculation. Here we present a typical example of 10 mole percent methanol solution. Figure 4 shows the position of 11 methanol molecules in 97 benzene molecules which are faded away from the figure. The three projections to the directions of *x*, *y* and *z* axes in the rectangular ordinate are shown for the 100,000th, 800,000th and 1,600,000th configurations obtained from MC run. Only those methanol molecules which assemble on all the three projections are self-associating. It is clear that no self-association is observed for the 100,000th configuration. With the advancement of MC run, methanol molecules tend to come together. It can be seen that only four methanol molecules remain monomeric already at the 800,000th configuration. As shown later, general aspect of the self-association of methanol is the same for the configurations after 1,000,000 MC steps. In accordance with such a cluster formation-like process, the potential energy of the system is observed to decrease to an equilibrium state. Here representative example of equiolar mixture is shown in Figure 5.

Structure of Solution

The Monte Carlo results can be used to examine the structure of each solution. Figure 6 shows equilibrium distributions of methanol molecules in the cell for the four solutions studied. For clear understanding of the situation, all the benzene molecules are eliminated in the graphical display. It is seen that about the half of methanol molecules are in the form of independent monomer state in 5 mol% methanol solution. As the methanol content increases, many methanol molecules tend to form self-associating complex. In the case of equimolar mixture, almost all the methanol molecules are self-associating. Moreover, the shape of self-associating polymer chan-

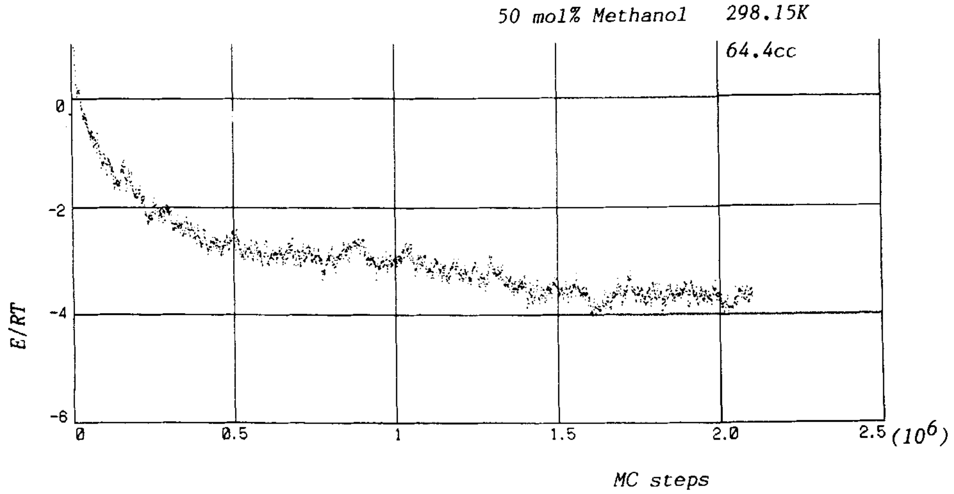
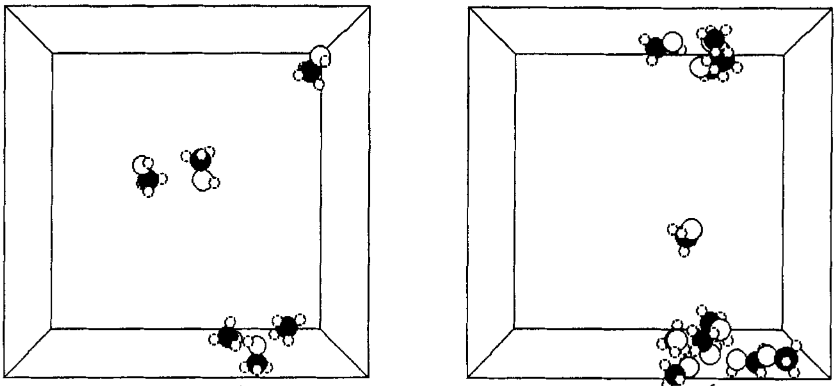
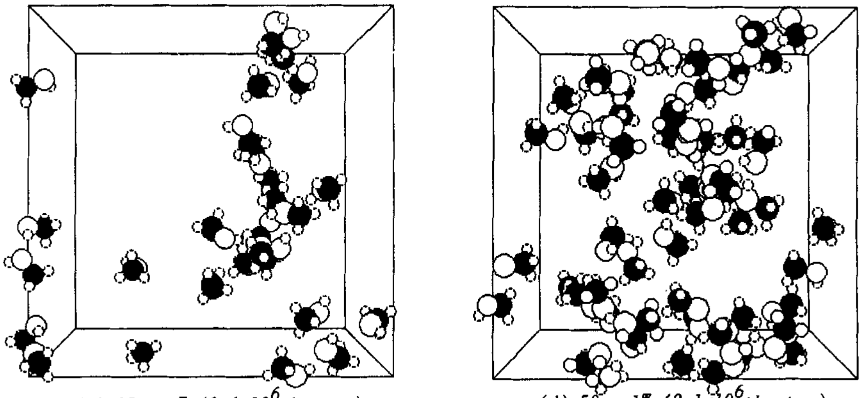


Figure 5 Potential energy change during the MC run for equimolar mixture.



(a) 5 mol% (2.6x10^{6}th step) (b) 10 mol% (1.6x10^{6}th step)



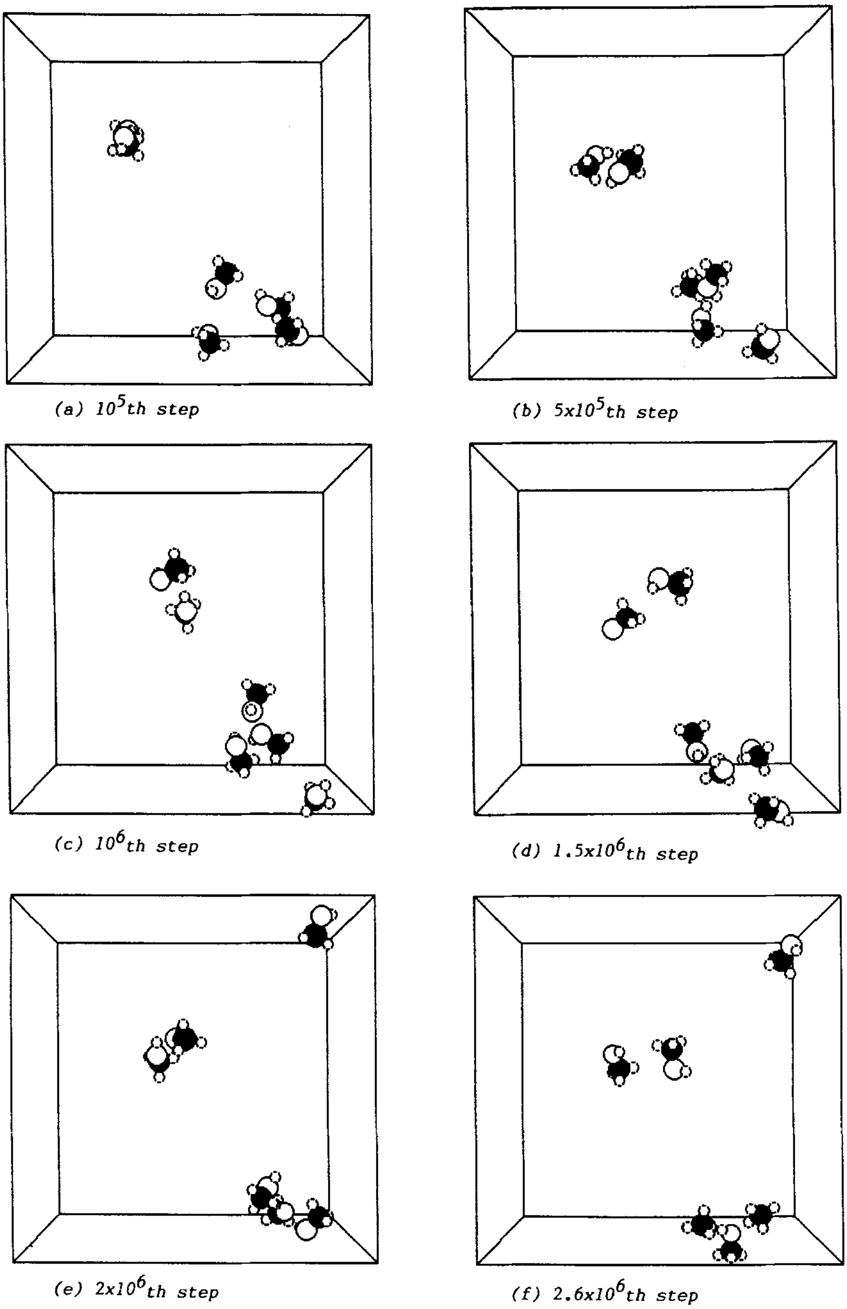
(c) 25 mol% (2.6x10^{6}th step) (d) 50 mol% (2.1x10^{6}th step)

Figure 6 Configurations of methanol molecules in the four solutions studied.

ges from spherical in 10 mole% solution to flexible chain-like in 25 mol% and equimolar solutions. Any one of the four figures just explained is simply each one particular configuration obtained by MC run. That they represent the configuration of molecules in each solution may be seen from the comparison of several configurations for 5 mol% methanol solution given in Figure 7. It is seen that, although self-associating complex changes its shape during the MC run, general characteristics of solution structure remains unchanged. The structure of solution can best be described by radial distribution functions (RDF). However, RDFs are not so informative when the number of molecules in question is rather small. Therefore, only those for the equimolar mixture are shown in Figure 8.

Distribution of Pair Interaction

In order to understand energetic aspect of the self-association of methanol, pair interaction distribution functions (PIDF) have been calculated for each solution. The results are shown as the four diagrams in Figure 9. In each diagram, a large peak with



(a) 10^5th step

(b) 5x10^5th step

(c) 10^6th step

(d) 1.5x10^6th step

(e) 2x10^6th step

(f) 2.6x10^6th step

Figure 7 Configurations of methanol molecules in 5 mol% solution at several time steps.

its center at the zero energy is, apart from the contribution from pairs with large separation, attributed to benzene-benzene and benzene-methanol interactions, while a broad peak between -10 and -25 kJ/mol for self-associating methanol molecules.

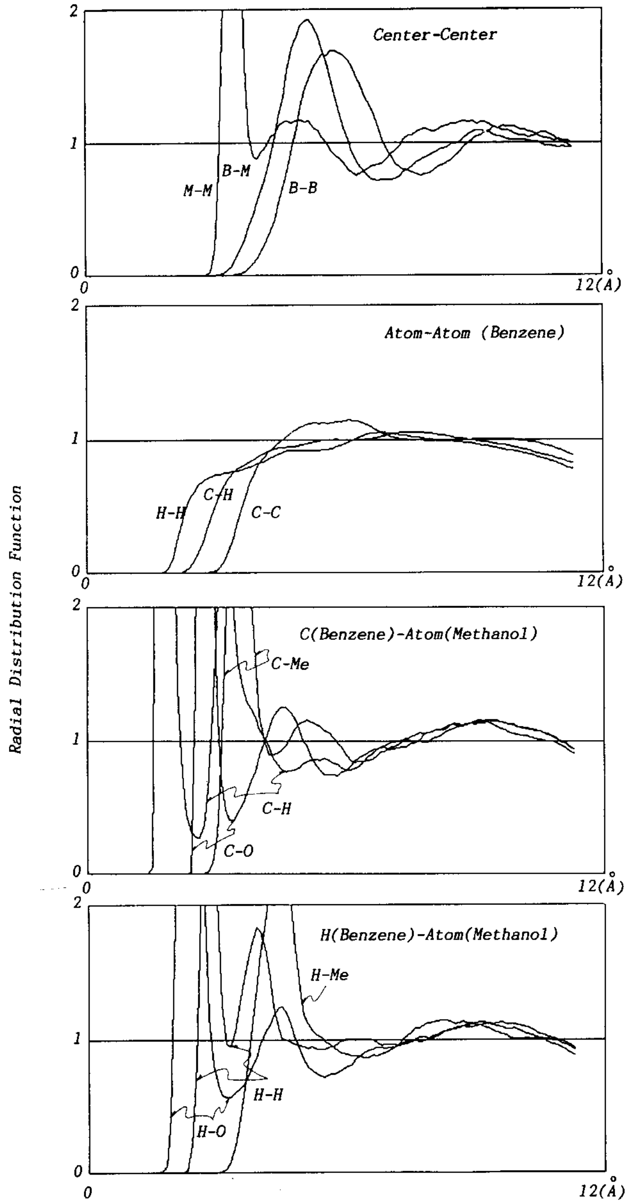


Figure 8 Several kinds of radial distribution (pair correlation) functions for equimolar mixture.

Because of insufficient statistics, the peak is by no means smooth. However, the presence of such a broad band suggests a loosely bonded complex consists of a large number of methanol molecules. We also call attention to the change in the PIDF for methanol-methanol pairs with the molar composition of methanol. Fundamental characteristics of the PIDF peak do not change, but we note that the center of the peak gradually shifts to higher energy (the absolute value) direction as the molar

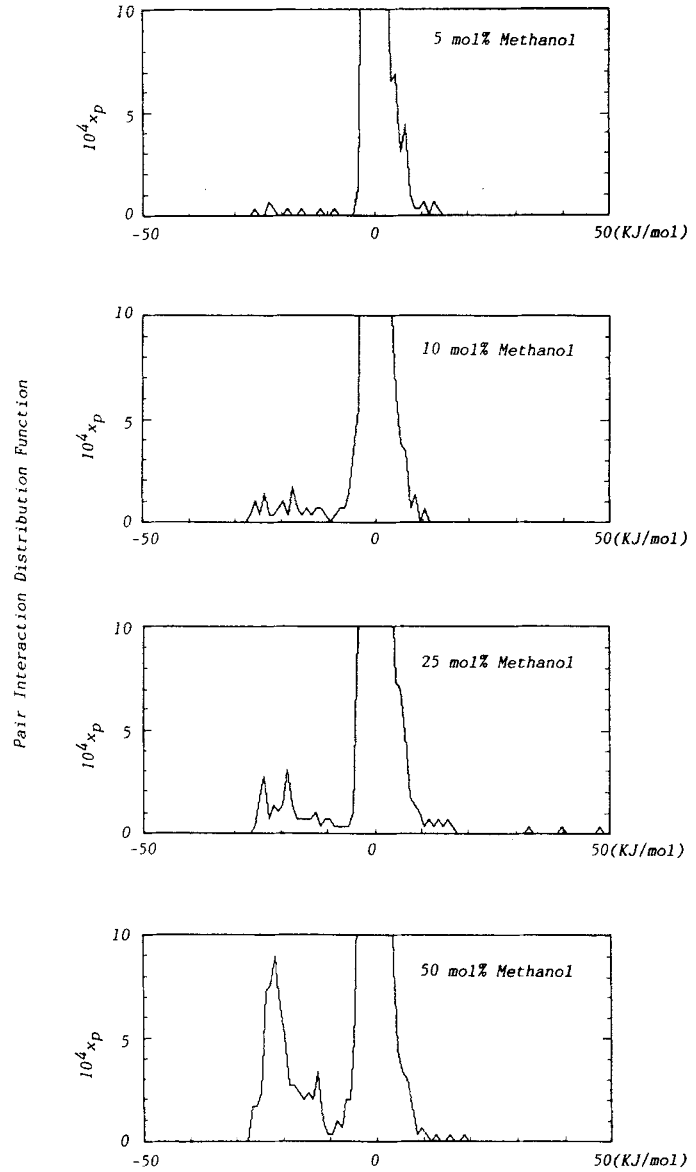


Figure 9 Pair interaction distribution functions for the four solutions studied.

composition of methanol increases. This means that hydrogen bonds become stronger as the size of associating complexes of methanol increases.

Monomer Fraction

It is estimated from the infrared spectral data that alcohol molecules exit as a monomer only in extremely dilute solutions of nonpolar molecules [2]. As the con-

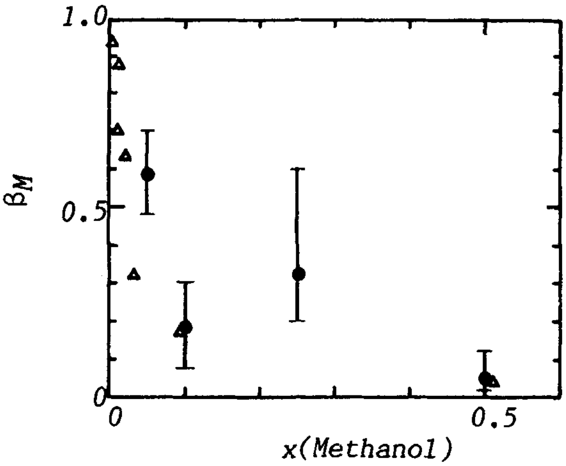


Figure 10 The fraction of methanol monomer β_M as a function of methanol content. ●: from MC (this work). △: from IR [2].

centration of alcohols increases, the self-association of alcohol proceeds and the fraction of monomers decreases rapidly. We can easily evaluate the monomer fraction and the averge number of methanol molecule in the self-associating complexes from the MC data as in Figures 10 and 11. The MC and IR data agree fairly well with each other. However, we note that the MC data show some irregularity between 10 and 25 mole per cent solutions and that the monomer fraction from MC simulation is generally somewhat larger than that from IR spectra [2].

CONCLUDING REMARKS

Monte Carlo calculations have been carried out for an equimolar benzene-rich mixture of benzene–methanol binary system. This is the first attempt at a computer

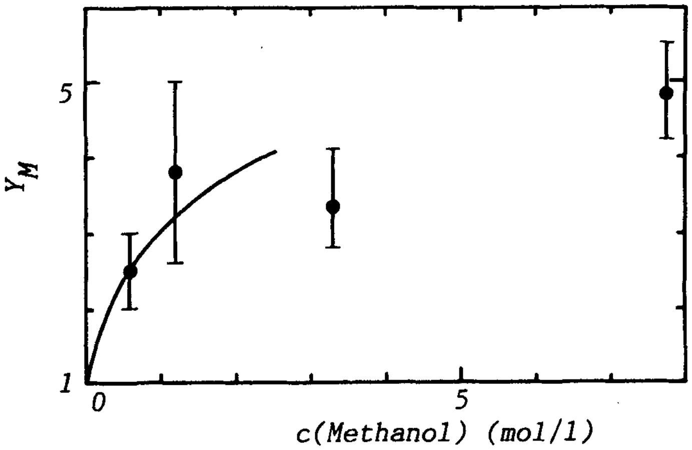


Figure 11 Average number Y_M of methanol in self-associating complex as a function of methanol concentration in mol/liter.

simulation of alcohol-nonpolar molecule systems in which one of components exhibits self-association owing to its ability to act both as proton donor and acceptor. It is confirmed that methanol molecules exhibit self-association, the degree of which increases with increasing the methanol content. The shape of the associating complex of methanol changes from sphere-like in dilute solutions to flexible chain type in concentrated solutions. The average hydrogen bond energy in the complex becomes larger as the size of complex increases. The phenomena in general observed in the present associated solutions are considered to be a reverese of the hydrophobic interaction in dilute aqueous solutions of nonpolar molecules [7]. The difference is that here the self-associating species have a stronger interaction. Thus, we propose that the phenomenon could be labelled as the "lyophobic interaction." However, contrary to the case of water as a solvent where the hydrophobic hydration is of special interest, there is no self-organization of solvents in the present case.

Further Monte Carlo calculations are in progress to cover the methanol-rich region as well as the two pure fluid states.

Acknowledgment

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