Molecular Dynamics Simulation Studies of Benzene, Toluene, and *p*-Xylene in NpT Ensemble: Thermodynamic, Structural, and Dynamic Properties

Ja Hun Kim and Song Hi Lee*

Department of Chemistry, Kyungsung University, Busan 608-736, Korea
Received October 31, 2001

In this paper we have presented the results of thermodynamic, structural, and dynamic properties of model systems for liquid benzene, toluene and *p*-xylene in an isobaric-isothermal (NpT) ensemble at 283.15, 303.15, 323.15, and 343.15 K using molecular dynamics (MD) simulation. This work is initiated to compensate for our previous canonical (NVT) ensemble MD simulations [*Bull. Kor. Chem. Soc.* **2001**, 23, 441] for the same systems in which the calculated pressures were too low. The calculated pressures in the NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. The first and second peaks in the center of mass g(r) diminish gradually and the minima increase as usual for the three liquids as the temperature increases. The three peaks of the site-site g_{C-C}(r) at 283.15 K support the perpendicular structure of nearest neighbors in liquid benzene. Two self-diffusion coefficients of liquid benzene *via* the Einstein equation and *via* the Green-Kubo relation are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene and *p*-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group. The friction constants calculated from the force auto-correlation (FAC) function with the assumption that the fast random force correlation ends at time which the FAC has the first negative value give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The friction constants calculated from the FAC's are always less than those obtained from the friction-diffusion relation which reflects that the random FAC decays slower than the total FAC as described by Kubo [*Rep. Prog. Phys.* **1966**, 29, 255].

Keywords : Molecular dynamics simulation, Benzene, Toluene, *p*-Xylene, NpT ensemble.

Introduction

In a previous paper[1] we reported the results of thermodynamic, structural and dynamic properties of liquid benzene, toluene, and *p*-xylene in a canonical (NVT) ensemble at 298.15 K by molecular dynamics (MD) simulations. The molecular model adopted for these molecules was a combination of the rigid body treatment for the benzene ring and an atomistically detailed model for the methyl hydrogen atoms. The various thermodynamic properties reflected that the intermolecular interactions become stronger as the number of methyl group attached into the benzene ring increases. However, the calculated pressures were too low in the NVT ensemble MD simulations. The pronounced nearest neighbor peak in the center of mass g(r) of liquid benzene at 283.15 K provided the interpretation that nearest neighbors tend to be perpendicular. Two self-diffusion coefficients of liquid benzene at 283.15 K calculated from MSD and VAC function were in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene also agreed well with the experimental ones for toluene in benzene and for toluene in cyclohexane.

In NVT MD simulations, the density of system is automatically determined from the fixed number of molecules and the fixed volume. When one considers the change of the density of system, ρ = N/V, the change of either the number of molecules N or the volume V is allowed. If the change of N is chosen, the simulation ensemble becomes a grand canonical ensemble (μVT), and the choice of the change of V means an isobaric-isothermal ensemble (NpT). Though the performance of MD simulations in NpT ensemble for molecular liquid is not easy, a μVT ensemble MD simulation involved with the creation and banishment of molecules is more difficult to carry out. Equations of motion for the NpT MD simulation of molecular liquids presented in the next section were derived by Evans.[2,3]

In this study we have chosen an NpT ensemble in order to carry out MD simulations for liquid benzene, toluene, and *p*-xylene at 283.15, 303.15, 323.15, and 343.15 K. The primary purpose of this work is to compensate for our previous NVT MD simulations,[1] and, secondly, to investigate the equilibrium thermodynamic properties, molecular structures, and diffusion coefficients and friction constants as a function of temperature.

This paper is organized as follows: In Section II, we present the molecular models and NpT MD simulation methods. We discuss our simulation results in Section III and present the concluding remarks in Section IV.

Molecular Models and NpT MD Simulation Methods

The molecular model used is the same as in the previous NVT MD simulation;[1] the benzene ring is assumed as a rigid-body, but three C-H bonds in the methyl groups of toluene ($C_6H_5CH_3$) and *p*-xylene ($CH_3C_6H_4CH_3$) are not assumed to be rigid. Simple harmonic oscillation potentials for C-H bond stretching and C-C-H and H-C-H bond angle

Table 1. Potential parameters for liquid benzene, toluene, and *p*-xylene

LJ parameters	σ (nm)	ε (kJ/mol)
C-C	0.3367	0.4056
C-H	0.2799	0.1722
H-H	0.2230	0.0731

bond stretching	r_e (nm)	K_0 (kJ/molnm^2)
C-H	0.110	147000

bond angle bending	θ_o (deg)	K_1 (kJ/mol · deg^2)	K_2 (kJ/mol · deg^3)
C-C-H	109.7	0.050209	0.000482
H-C-H	107.9	0.050209	0.000482

torsional	ϕ_o (deg)	K_3 (kJ/mol)
C-C-C-H	180	11.72

bending in the methyl group are used, and the methyl groups are rotating according to a torsional potential. Potential parameters for the molecular model are given in Table 1.

The equation of translational motion for these systems are

$$\dot{\mathbf{r}}_\mathbf{i} = \mathbf{p}_\mathbf{i} + \dot{\varepsilon}\mathbf{r}_\mathbf{i} \tag{1}$$

$$\dot{\mathbf{p}}_\mathbf{i} = \mathbf{F}_\mathbf{i} - \dot{\varepsilon}\mathbf{p}_\mathbf{i} - \alpha_t\mathbf{p}_\mathbf{i}, \tag{2}$$

where $\mathbf{F}_i$ is the force acting on molecule i. The translational temperature constant parameter is given by Gaussian iso-kinetics:[4]

$$\alpha_t = \frac{\sum_i^N \mathbf{p}_\mathbf{i} \cdot \mathbf{F}_\mathbf{i}}{\sum_i^N p_i^2} - \dot{\varepsilon} \tag{3}$$

and the dilation rate is given by

$$\dot{\varepsilon} = -\frac{\sum_{i \neq j}^N (\mathbf{r_{ij}} \cdot \mathbf{p_{ij}})(\Phi''_{ij} + \Phi'_{ij}/r_{ij})}{m\sum_{i \neq j}^N r_{ij}^2(\Phi''_{ij} + \Phi'_{ij}/r_{ij}) + 9pV}. \tag{4}$$

For polyatomic molecules with different site-site atomic potentials, the potential $\Phi(r)$ is averaged from the site-site atomic potentials. For benzene, $\Phi(r)$ becomes[5]

$$\Phi(r) = [36\phi_1(r) + 72\phi_2(r) + 36\phi_3(r)]/144, \tag{5}$$

where $\phi_1(r)$ is the C-C Lennard-Jones potential, $\phi_2(r)$ the C-H, and $\phi_3(r)$ the H-H.

The equations of rotational motion about the center of mass for molecular liquids using quaternions[6,7] are as follows:[8]

$$\dot{L}_i = T_i - \alpha_r L_i, \tag{6}$$

$$L_i^p = A_i \cdot L_i, \tag{7}$$

$$\omega_{ik}^p = L_{ik}^p/I_k, \; k = x, y, z, \tag{8}$$

$$\begin{pmatrix} \dot{q}_{i1} \\ \dot{q}_{i2} \\ \dot{q}_{i3} \\ \dot{q}_{i4} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -q_{i3} & -q_{i4} & q_{i2} & q_{i1} \\ q_{i4} & -q_{i3} & -q_{i1} & q_{i2} \\ q_{i1} & q_{i2} & q_{i4} & q_{i3} \\ -q_{i2} & q_{i1} & -q_{i3} & q_{i4} \end{pmatrix} \begin{pmatrix} \omega_{ix}^p \\ \omega_{iy}^p \\ \omega_{iz}^p \\ 0 \end{pmatrix} \tag{9}$$

where T_i is the torque on molecule i in the laboratory frame, and L_{ij}^p and ω_{ik}^p the angular momenta and angular velocities of molecule i in its principle axis frame, respectively. A_i is the rotation matrix which transforms vectors form the laboratory to principal axis frame of molecule i, and q_{ik} are the quaternions related to the Euler angles describing the orientation of molecule i and space. The rotational temperature constraint parameter α_r is given by

$$\alpha_r = \sum_i^N L_i \cdot T_i / \sum_i^N L_i^2. \tag{10}$$

Since the volume of the system changes, the usual boundary conditions cannot be used. If molecule i moves outside the simulation box, its image enters through the opposing face in the usual way, but all the higher derivatives of $\mathbf{r}_i$ and $\dot{\varepsilon}$ are changed in this imaging procedure and they should be recalculated.[5]

The next consideration is the so called long-range correction due to the spherical cutoff of the potential which is a tail correction estimating the contribution from pairs of particles whose separation is greater than the cut-off distance (r_c). These corrections are calculated by assuming that the radial distribution function g(r) is unity for $r > r_c$. If the distance between any two centers of mass is within this distance, all the interactions between the atomic sites of two molecules are considered. The correction is for the potential energy[9]

$$E_{LRC}/N = \frac{\rho}{2}\int_{r_c}^\infty \Phi(r)g(r)4\pi r^2 dr, \tag{11}$$

for the pressure

$$p_{LRC} = -\frac{\rho^2}{6}\int_{r_c}^\infty r\Phi'(r)g(r)4\pi r^2 dr, \tag{12}$$

which is especially important in the NPT ensemble simulation, and for the denominator of Eq. (4)

$$D_{LRC} = \frac{\rho^2}{2}\int_{r_c}^\infty [r^4\Phi''(r) + r^3\Phi'(r)]g(r)4\pi r^2 dr, \tag{13}$$

where $\Phi(r)$ is given by Eq. (5).

The usual periodic boundary condition in the *x*-, *y*-, and *z*-directions and minimum image convention for pair potential were applied. A spherical cut-off of radius $R_c = 1.25$ nm was employed for the pair interactions. For the integration over time, we adopted Gear's fifth order predictor-corrector algorithm[10] with a time step of 0.0002 ps. MD simulation runs of about several 150,000 time steps were needed for each liquid molecular system to reach equilibrium. The equilibrium properties were then averaged over 5 blocks of 150,000 time steps for a total of 750,000 time steps, and the configurations of molecules were stored every 10 time steps for analyses of structural and dynamic properties.

Results and Discussion

Thermodynamic properties. Thermodynamic properties for liquid benzene, toluene and *p*-xylene at 283.15, 303.15, 323.15, and 343.15 K obtained from our MD simulations are

Table 2. Thermodynamic and structural properties for liquid benzene

properties	T = 283.15	303.15	323.15	343.15
pressure (atm)	4.18	4.54	5.17	9.31
volume (nm^3)	15.6	16.0	16.4	16.7
inter LJ energy (kJ/mol)	−31.8	−30.8	−29.8	−28.9
inter elec. energy	−1.92	0.11	1.93	3.15

Table 3. Thermodynamic and structural properties for liquid toluene

properties	T = 283.15	303.15	323.15	343.15
pressure (atm)	4.32	4.45	4.31	5.17
volume (nm^3)	16.2	16.4	16.7	17.0
inter LJ energy (kJ/mol)	−42.0	−41.1	−40.0	−39.2
inter elec. energy	6.7	8.0	9.5	11.6
C-H stretching energy	0.129	0.152	0.178	0.168
C-C-H and H-C-H angle bending energy	1.04	1.13	1.24	1.23
% of C-C-C-H *trans*	50.0	50.1	49.9	50.2
total barrier crossing T-G*	26184	28146	29472	30261
G-T	26180	28137	29472	30263

*Total of 750,000 time steps.

Table 4. Thermodynamic and structural properties for liquid *p*-xylene

properties	T = 283.15	303.15	323.15	343.15
pressure (atm)	5.12	4.89	4.95	5.51
volume (nm^3)	21.4	21.8	22.3	22.9
inter LJ energy (kJ/mol)	−41.8	−40.3	−39.1	−37.7
inter elec. energy	17.5	17.0	16.5	15.9
C-H stretching energy	0.063	0.072	0.082	0.079
C-C-H and H-C-H angle bending energy	1.14	1.25	1.36	1.37
% of C-C-C-H *trans*	49.9	50.0	49.9	49.8
total barrier crossing T-G*	60363	62250	63945	65544
G-T	60367	62237	63940	65555

*Total of 750,000 time steps.

listed in Tables 2, 3, and 4, respectively. The calculated pressures in our NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. In the previous NVT ensemble MD simulations,[1] the volumes for benzene, toluene and *p*-xylene were fixed as 17.7, 21.2, and 24.6 nm^3 respectively at 298.15 K which were apparently overestimated, and the calculated pressures in the NVT MD[1] were too low.

The intermolecular energy increases negatively as the number of methyl group increases from liquid benzene to liquid toluene, and decreases negatively from liquid toluene to liquid *p*-xylene, which is the opposite trend to what we observed in the previous NVT ensemble MD simulations.[1] This reflects that the calculated intermolecular energy depends on the volume of the system very much. When compared with the experimental solvation enthalpies of vapors condensing into liquids at 298.15 K[11] which are −32.5, −36.6, and −41.1 kJ/mol for benzene, toluene and *p*-xylene, respect-

ively, the intermolecular energies for benzene and toluene are in good agreement but not for *p*-xylene.

The C-H bond stretching and the C-C-H and H-C-H bond angle bending energies of both liquid toluene and *p*-xylene increase roughly with the temperature. This reflects that the steric effect becomes larger and repels each other, which contributes to the larger repulsive interactions of the bond stretching and the bond angle bending potential energies, as the temperature increases. However, the values of the bond stretching length and bond bending angle are remained constant (not shown).

Toluene has two dihedral states which are doubly imposed torsional rotational potential on the same bond, and *p*-xylene has four dihedral states of which each two are doubly imposed torsional rotational potential on the same bonds. The average % of C-C-C-H *trans* and the total barrier crossing T-G and G-T in toluene are related to the doubly imposed dihedral state in the way that if one dihedral state is in *gauche*, then the other should be in *trans*, or *vice versa*. That is why the average C-C-C-H torsional energy is the same as K_3 since $\phi_2 = 180°-\phi_1$ for a given dihedral angle ϕ_1 and $V_{average}(\phi) = [V(\phi_1) + V(\phi_2)]/2 = K_3$. The total barrier crossing T-G and G-T in toluene and *p*-xylene in our NpT ensemble MD simulations are higher than those in the previous NVT MD(about 25,510 for toluene and 60,140 for *p*-xylene, respectively, in 750,000 time steps at 298.15 K).[1]

**Structural properties**. The radial distribution function, g(r), is defined as

$$g(r) = \frac{1}{\rho_0}\left\langle\frac{N(r, \Delta r)}{V(r, \Delta r)}\right\rangle \qquad (14)$$

where ρ_0 is the bulk density, $N(r, \Delta r)$ is the number of molecules in a shell which is between $r − \Delta r/2$ and $r + \Delta r/2$ from the center of a molecule with $\Delta r = 0.005$ nm, $V(r, \Delta r)$ is the volume of the shell, and $\langle\cdots\rangle$ indicates the isothermal-isobaric ensemble (NpT) average. The center of mass g(r) of liquid benzene, toluene, and *p*-xylene at 283.15, 303.15, 323.15, and 343.15 K are shown in Figures 1-3, respectively, and the site-site $g_{C-C}(r)$ of liquid benzene, toluene, and *p*-
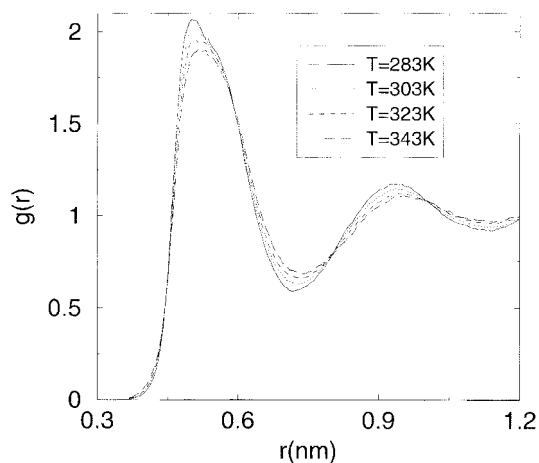
Figure 1. Center of mass radial distribution function for liquid benzene at 283.15, 303.15, 323.15, and 343.15 K.

450   *Bull. Korean Chem. Soc.* **2002**, Vol. 23, No. 3

Ja Hun Kim and Sone Hi Lee
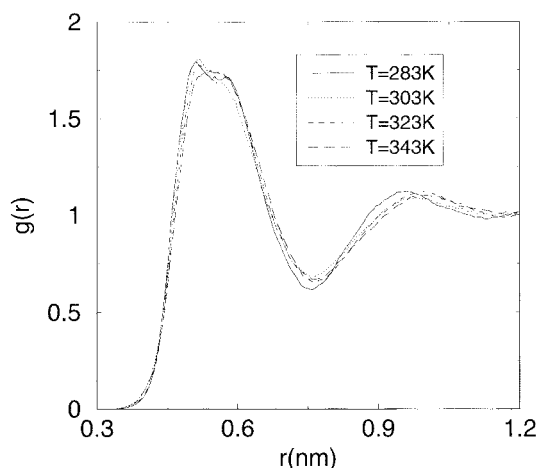
Figure 2. Center of mass radial distribution function for liquid toluene at 283.15, 303.15, 323.15, and 343.15 K.
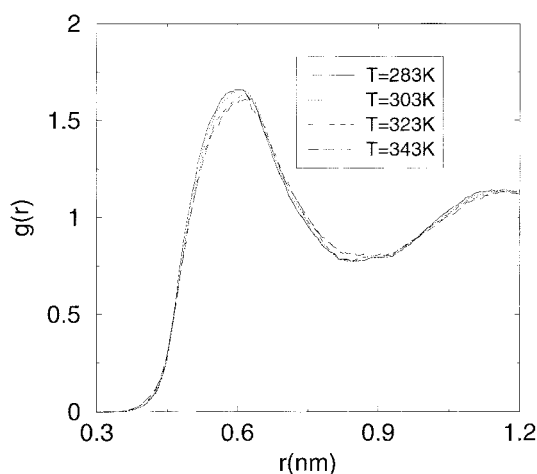

Figure 3. Center of mass radial distribution function for liquid *p*-xylene at 283.15, 303.15, 323.15, and 343.15 K.

xylene at 283.15 K is also shown in Figure 4.

As the temperature increases, the first and second peaks in the center of mass g(r) diminish gradually and the minima increase as usual for the three liquids. When compared with the center of mass g(r) in the previous NVT MD simulations[1] at 298.15 K, the peaks diminish and the minima increase as if the temperature increases due to the large volumes of systems used in the NVT MD. It is also observed that the successive addition of methyl group into the benzene ring causes the width of the first solvation shell larger and the first peak lower, which indicates the variance of the distance between centers of mass as the molecular weight increases.

The site-site $g_{C-C}(r)$ of liquid benzene at 283.15 K in Figure 4 has three peaks at 0.39, 0.49, and 0.60 nm unlike an outshoot at 0.40 nm and two peaks at 0.48 and 0.60 nm in the previous NVT MD simulations.[1] The study of the scattering of X-rays of liquid benzene at 298.15 K has reported three peaks.[12] The RISM results[13] also showed the same feature for $g_{C-C}(r)$ of liquid benzene. In the assumption that
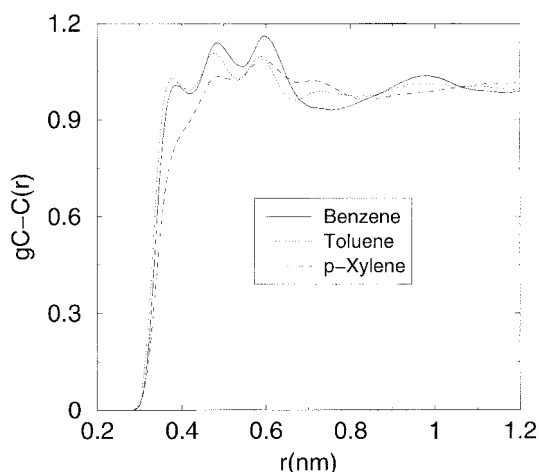

Figure 4. Site-site radial distribution function $g_{C-C}(r)$ for liquid benzene, toluene, *p*-xylene at 283.15 K.

nearest neighbors in liquid benzene were parallel to one another ('stacked' configuration), the relatively free rotation about its six-fold rotation axis would randomize the separation between C-C sites and as a result, the site-site $g_{C-C}(r)$ would give a single peak. The three peaks of the site-site $g_{C-C}(r)$ at 283.15 K support the perpendicular structure of nearest neighbors in liquid benzene.

The center of mass distance between two nearest neighbors in liquid benzene is approximately 0.50 nm as seen from Figure 1. In the configuration that a carbon atom of benzene molecule approaches perpendicularly to the center of mass of the other lying benzene molecule, among 36 total C-C pairs, 6 C-C pairs are at distance 0.39 nm, 2 at 0.43, 0.50, and 0.57, and 4 at 0.45, 0.49, 0.59, 0.61, 0.63, and 0.66. When two neighbor carbon atoms approaches perpendicularly to the center of mass of the other lying benzene molecule, 2 at 0.39, 0.43, 0.50, 0.57, and 0.66, 4 at 0.40, 0.42, 0.52, 0.56, and 0.65, and 6 at 0.63. The first configuration gives a better explanation for three peaks at 0.39, 0.49, and 0.60 nm in the site-site $g_{C-C}(r)$ of liquid benzene at 283.15 K in Figure 4.

As the number of methyl group increases, the three peaks in liquid benzene are still existed but lowered in liquid toluene as in Figure 4 unlike two peaks in the previous NVT MD study,[1] a fourth peak at about 0.7 nm appeared in liquid toluene and *p*-xylene, and the first peak is completely disappeared in liquid *p*-xylene. Considering the first configuration above with the methyl group farthest from the center of mass of the other benzene molecule, it is easily understood the three peaks are not changed and the fourth peak is related to the methyl group. In the site-site $g_{C-C}(r)$ of liquid *p*-xylene at 283.15 K in Figure 4, the first peak is disappeared and the fourth peak becomes clearer, which reflects a large possibility of the closeness of the methyl groups to the center of mass of the other benzene ring.

Dynamic properties. As dynamic properties, we consider self-diffusion coefficients and friction constants of liquid benzene, toluene, and *p*-xylene. The mean square displacements (MSD's) obtained from our MD simulations for liquid benzene only are shown in Figure 5. But MSD's for liquid

MD Simulation of Benzene in NpT Ensemble

Bull. Korean Chem. Soc. **2002**, Vol. 23, No. 3   451
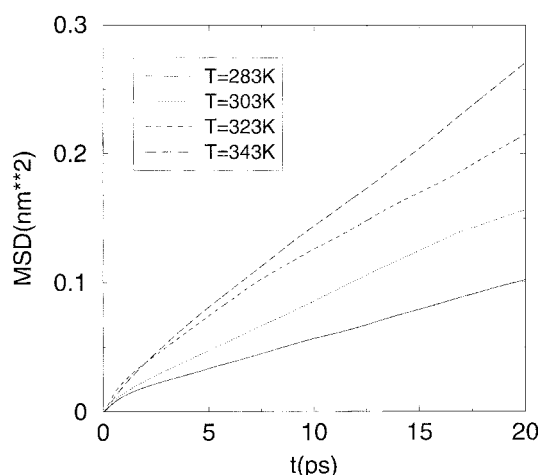
Figure 5. Mean square displacement as a function of time for liquid benzene, toluene, and *p*-xylene at 283.15 K.

Figure 6. Force auto-correlation functions as a function of time for liquid benzene, toluene, and *p*-xylene at 283.15 K.

toluene and *p*-xylene and velocity auto-correlation functions (VAC's) for liquid benzene, toluene, and *p*-xylene are not shown. Self-diffusion coefficients can be calculated from MSD's using Einstein relation:

$$D_s = \frac{1}{6}\lim_{t \to \infty}\frac{d < |\mathbf{r}(t) - \mathbf{r}(0)|^2}{dt}. \tag{15}$$

Another route for self-diffusion coefficients calculated from the VAC's is the Green- Kubo relations. The self-diffusion coefficient can be separated into two parts according to
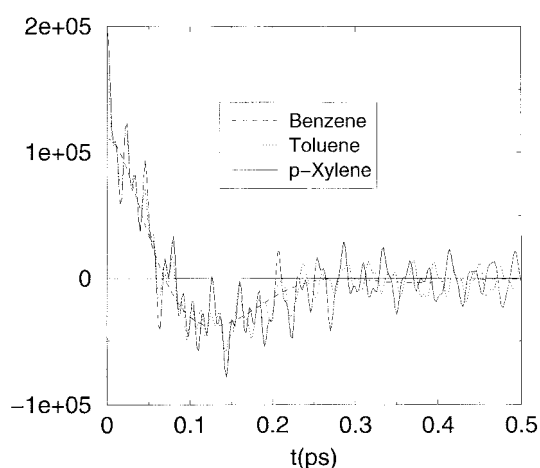
$$D_s = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt = \frac{1}{3}\langle v^2 \rangle A = \frac{3kT}{m}A, \tag{16}$$

where $\mathbf{v}_i(t)$ is the center of mass velocity of a single molecule. Since $m\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0)\rangle = mv^2 = 3kT$, the integration value of the normalized VAC function, A, is given by

$$A = \frac{1}{3}\int_0^\infty \frac{\langle v(0) \cdot v(\tau)\rangle}{\langle v(0) \cdot v(0)\rangle}d\tau. \tag{17}$$

Self-diffusion coefficients of the three liquids calculated from the slopes of the MSD's between 5.0 and 20.0 ps and from the average of the integration of the VAC's from t = 0 ps to 2.5 ps up to 20.0 ps are listed in Table 5. The MD simulation study of benzene and its fluorinated derivatives at 300 K by Caba o *et al.*[14] reported 1.2×10^{-9} m²/s as the self-diffusion coefficient of benzene, but the experimental measures[15-18] are comparable to our results. It is very fortuitous that both self-diffusion coefficients obtained from MSD and VAC of our MD simulations are in overall agreement with the experimental results.

Unfortunately there is no experimental result for the self-

diffusion coefficients of liquid toluene and *p*-xylene. The experimental diffusion coefficients, however, in different solvent are available for toluene. For example, 1.85 for toluene in benzene, 1.57 in cyclohexane, 3.72 in hepatne, 4.21 in hexane, and 0.85×10^{-9} m²/s in water[19] at 298.15 K. When compared with these experimental results for toluene in benzene and for toluene in cyclohexane, our MD simulation results for the self-diffusion coefficients of liquid toluene also provide an excellent agreement. The self-diffusion coefficients of liquid *p*-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group.

A friction constant is obtained from the time integral of the force auto-correlation function:[20,21]

$$\zeta = \frac{1}{\tau_r} = \frac{1}{kT}\int_0^\tau dt \langle \mathbf{f}_i(t) \cdot \mathbf{f}_i(0)\rangle, \tag{18}$$

where $\mathbf{f}_i(t) = \mathbf{F}_i(t) - \langle\mathbf{F}_i(t)\rangle$, $\mathbf{F}_i(t)$ is the total force exerted on molecule i, and $_r$ is the macroscopic relaxation time of the FAC.[21] The force auto-correlation functions (FAC's) obtained from our MD simulations for liquid benzene, toluene, and *p*-xylene at 283.15 K only are shown in Figure 6. The FAC function for liquid benzene shows a well-behaved smoothly decaying curve, while those for liquid toluene and *p*-xylene are oscillating ones probably due to the interaction of methyl groups but tend to decay slowly. The initial decay is very rapid, occurring in a time ~0.3 ps, while a subsequent long tail decays only after several ps (not shown). It is notorious that the calculation of friction constant from the force auto-correlation function is very hard due to the non-decaying long-time tails.

Table 5. Self-diffusion coefficients (D_s, 10^{-9} m²/s) for liquid benzene, toluene, and *p*-xylene calculated from MSD's and VAC's. The numbers in parenthesis are D_s from VAC's and the value of A (10^{-2} ps) in Eq. (17)

Molecules	T = 283.15	303.15	323.15	343.15
benzene	0.76(0.72, 0.79)	1.25(1.19, 1.15)	1.52(1.53, 1.48)	2.09(2.16, 2.09)
toluene	0.67(0.61, 0.79)	0.92(0.90, 1.10)	1.24(1.21, 1.38)	1.67(1.62, 1.85)
p-xylene	0.51(0.52, 0.78)	0.75(0.76, 1.06)	1.01(1.00, 1.31)	1.32(1.33, 1.76)

Table 6. Friction constants (ζ, kg/mol ps) for liquid benzene, toluene, and *p*-xylene obtained from the FAC's using Eq. (18) and from Eq. (19) (in parenthesis)

Molecules	T = 283.15	303.15	323.15	343.15
benzene	1.85 (3.10)	1.76 (2.02)	1.67 (1.77)	1.62 (1.37)
toluene	1.96 (3.51)	1.89 (2.74)	1.81 (2.17)	1.75 (1.71)
p-xylene	2.13 (4.62)	2.03 (3.36)	1.96 (2.66)	1.87 (2.16)

As Kubo pointed out in his "fluctuation-dissipation theorem",[21] the correlation function of random force R will decay in a time interval of τ_c (microscopic time or collision duration time), whereas that of the total force F has two parts, the short time part or the fast similar to that of the random force and the slow part which should just cancel the fast part in the time integration (Kubo approximately described these two FAC's in his original papers, see Figure 2 in Ref. 21). This means that the time integral of Eq. (18) up to $\tau = \infty$ is equal to zero. The time integral in Eq. (18) attains a plateau value for τ satisfying $\tau_c \ll \tau \ll \tau_r$, if the upper limit of the time integral, Eq. (18), is chosen that $\tau_c \ll \tau \ll \tau_r$ because the slow tail of the correlation function is cut off. However, we were unable to get the plateau value in the running time integral of the force auto-correlation function.

Kubo suggested above that the friction constants should be obtained from the random force auto-correlation (FAC) function not from the total FAC and that there exists a difficulty to separate the random force part from the total force. We could obtain the friction constants by the time integral of the total FAC with choosing the upper limit of as the time which the FAC has the first negative value by assuming that the fast random force correlation ends at that time. The friction constant is related to the diffusion coefficient D using Einstein relation, Eq. (15):

$$\zeta = kT/D. \qquad (19)$$

Table 6 contains the friction constants obtained from the time integral of the FAC using Eq. (18) and from Eq. (19) with D_s obtained from MSD's in Table 5. Both the friction constants give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The calculated friction constants from the FAC's using Eq. (18) are always less than those obtained from Eq. (19) except liquid toluene at 343.15 K which reflects that the random FAC decays slower than the total FAC as described by Kubo (see Figure 2 in Ref. 21), but the overall agreement is quite good in the same magnitude of order.

Conclusion

In this paper, we have presented the results of thermodynamic, structural, and dynamic properties of model systems for benzene, toluene and *p*-xylene in an isobaric-isothermal (NpT) ensemble at 283.15, 303.15, 323.15, and 343.15 K using equilibrium molecular dynamics (EMD) simulation. This work is initiated to compensate for our previous NVT MD

simulations[1] for the same systems at 298.15 K in which the calculated pressures were too low. The calculated pressures in the NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. The first and second peaks in the center of mass g(r) diminish gradually and the minima increase as usual for the three molecules as the temperature increases. It is also observed that the successive addition of methyl group into the benzene ring causes the width of the first solvation shell larger and the first peak lower, which indicates the variance of the distance between centers of mass as the molecular weight increases. The three peaks of the site-site $g_{C-C}(r)$ at 283.15 K support the perpendicular structure of nearest neighbors in liquid benzene. Two self-diffusion coefficients of liquid benzene calculated from MSD *via* the Einstein equation and VAC function *via* the Green-Kubo relation are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene and *p*-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group. We have calculated the friction constants of liquid benzene, toluene, and p-xylene from the force auto-correlation (FAC) function with the assumption that the fast random force correlation ends at time which the FAC has the first negative value. Both the friction constants give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The calculated friction constants from the FAC's are always less than those obtained from the friction-diffusion relation (Eq. (19)) except liquid toluene at 343.15 K which reflects that the random FAC decays slower than the total FAC as described by Kubo.

References

1. Kim, J. H.; Lee, S. H. *Bull. Korean Chem. Soc.* **2001**, *23*, 441.
2. Evans, D. J.; Morriss, G. P. *Chem. Phys.* **1983**, *77*, 63.
3. Evans, D. J.; Morriss, G. P. *Comput. Phys. Repts.* **1984**, *1*, 297.
4. (a) Evans, D. J.; Hoover, W. G.; Failor, B. H.; Moran, B.; Ladd, A. J. C. *Phys. Rev.* A **1983**, *28*, 1016. (b) Simmons, A. D.; Cummings, P. T. *Chem. Phys. Lett.* **1986**, *129*, 92.
5. Lee, S. H.; Kim, H. S.; Pak, H. *J. Chem. Phys.* **1992**, *97*, 6933.
6. Evans, D. J. *Mol. Phys.* **1977**, *34*, 317.
7. Evans, D. J.; Murad, S. *Mol. Phys.* **1977**, *34*, 327.
8. Cummings, P. T.; Varner, Jr. T. L. *J. Chem. Phys.* **1988**, *89*, 6391.
9. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press.: Oxford, 1987; p 64.
10. Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equation*; Prentice-Hall: Englewood Cliffs, NJ, 1971.
11. Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016.
12. Narten, A. H. *J. Chem. Phys.* **1968**, *48*, 1630.
13. Lowden, L. J.; Chandler, D. *J. Chem. Phys.* **1974**, *61*, 5228.
14. Cabaço, M. I.; Danten, Y.;. Besnard, M.; Guissani, Y.; Guillot, B *J. Phys. Chem. B* **1997**, *101*, 6977.
15. Falcone, D. R.; Douglass, D. C.; McCall, D. W. *J. Phys. Chem.* **1967**, *71*, 2754.

16. Graupner, K.; Winter, E. R. S. *J. Chem. Soc.* **1952**, 1145.
17. Hiraoka, H.; Osugi, J.; Jono, W. *Rev. Phys. Chem. Japan* **1958**, *28*, 52.
18. Rathbun, R. E.; Babb, A. L. *J. Phys. Chem.* **1961**, *65*, 1072.
19. Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, 6th Ed.; 1969; Vol. II/5a.
20. Ciccotti, G.: Ferrario, M.: Hynes, J. T.: Kapral, R. *J. Chem. Phys.* **1990**, *93*, 7137.
21. Kubo, R. *Rep. Prog. Phys.* **1966**, *29*, 255.