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Intra- and Inter-molecular Potential Parameters for Molecular Dynamics Simulation of Benzene and Cyclohexane Mixture

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Intra- and inter-molecular potential parameters have been newly derived to calculate the density and the self-diffusion coefficients of benzene, cyclohexane and their mixtures by molecular dynamics (MD) simulation using a six-center Lennard-Jones model. First, the validity of new parameters was examined in comparison with the reference experimental densities of pure components. Then, these parameters were adopted to the simulation of a benzene and cyclohexane mixture. Since simple combining rules (Lorentz–Berthelot) underestimated the density of the mixture, a concentration-dependent interaction parameter was newly introduced to predict the density of the mixture. The agreement between the experimental data and the simulated self-diffusion coefficients of benzene and cyclohexane in their mixture were improved by introducing the concentration-dependent interaction parameter.

Introduction

The physical properties of the mixture of cyclic components such as benzene and cyclohexane are important in the process design of an organic hydride system used in hydrogen storage. The equilibrium and transport properties of a mixture of cyclic compounds mixture depend on their interaction and conformation, and their correlations have been investigated by several research groups. Sun *et al.* (1988) and Beg *et al*. (1993) measured the densities of benzene, cyclohexane and alcohols or hydrocarbons. Beg *et al*. (1994) measured the densities of benzene+cyclohexane mixtures. Sanni *et al.* (1971) and Sanni and Hutchison (1973) reported mutual diffusion coefficients and densities for binary organic liquid mixtures. Jonas *et al*. (1980) discussed the density effect on the transport properties of cyclohexane. Rodwin *et al*. (1965) also reported mutual diffusion coefficients for binary organic liquid mixtures. Mills (1965) measured the intradiffusion coefficients of benzene and cyclohexane at 25℃ and derived the frictional coefficients.

Molecular simulation has been widely applied to estimate physical properties owing to a rapid development of high-speed computers. In particular, molecular dynamics (MD) simulation is a powerful tool to calculate the transport properties, such as diffusion coefficient and viscosity. The MD simulations of the diffusion coefficient by some molecular models under supercritical conditions were performed by Higashi *et al.* (2005, 2010), and the density of the system affected the simulated results of diffusion coefficients. The force fields for potential parameters of organic molecules in MD simulations, such as UNIVERSAL proposed by Casewit *et al.* (1992) and DREIDING proposed by Mayo *et al*. (1990), have been proposed to calculate many properties. The optimized potential functions for liquid simulations (OPLS) proposed by Jorgensen *et al.* (1984), the modified potential function (SKS (Smith *et al.*; 1995) and SMMK (Siepmann *et al.*, 1997) and TraPPE force field (Martin and Siepmann, 1998, 1999; Chen and Siepmann, 1999; Wick *et al.*, 2000) were also proposed for calculation of the properties of hydrocarbons such as normal and branched alkanes. TraPPE force field was developed for other compounds. Dysthe *et al*. (1999a, 1999b, 2000) applied SMMK and other potential parameters to the calculation of transport properties for alkanes by equilibrium MD simulations. However, the application of MD simulation and quantitative discussion to the mixture of cyclic compounds have been limited due to the complex behavior of these systems.

Schaink *et al.* (1993) calculated the transport coefficients of liquid benzene+cyclohexane mixtures by MD simulation using rigid molecules of the six-center Lennard-Jones model.

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They were successful only in qualitatively describing the concentration dependences of thermal conductivity and shear viscosity, and yet the diffusion coefficients were calculated only for two conditions. Furthermore, since they used bond lengths larger than the literature values, their size and energy parameters were different from those used by the other researchers. Pan *et al*. (2007) performed molecular dynamics simulation for the diffusion behavior of benzene and cyclohexane molecules in poly(vinyl alcohol)-graphite hybrid membranes. Zhang and Müller-Plathe (2005) adopted reverse non-equilibrium molecular dynamics simulation to calculate the Soret coefficients in a liquid benzene and cyclohexane mixture. Errington and Panagiotopoulos (1999) proposed intermolecular potential models for benzene and cyclohexane. They used the Buckingham exponential-6 intermolecular potential function for the grand canonical Monte Carlo simulation to calculate the phase behavior of the system. Milano and Müller-Plathe (2004) discussed thermodynamics and structure form atomistic simulations for benzene and cyclohexane mixtures. Kim and Lee (2002) applied canonical (*NVT*) ensemble MD simulation to benzene and its derivatives. The self-diffusion coefficients were calculated by the mean square displacement (MSD) and the velocity autocorrelation function (VAF). Applicable models to predict the transport properties of s benzene+cyclohexane mixture have not been discussed over a wide range of mole fraction.

In this work, new intra- and inter-molecular potential parameters of benzene and cyclohexane for flexible six-center Lennard-Jones (12-6) model are presented. The MD simulations for benzene, cyclohexane and their mixtures were performed presuming a mixture of flat and distorted molecules. In order to confirm the validity of new parameters, the densities of pure components at 283–313 K were calculated. The concentration dependence of interaction parameters was introduced for the simulation of mixture. The self-diffusion coefficients for cyclohexane and benzene in their mixture were also calculated from the MSD of each component using the Einstein equation. The calculated results of density and self-diffusion coefficient were compared with the experimental results of references.

1. Simulation Method

1.1 Model and potential function

COGNAC 7.1.1 in OCTA2010 [http://www.octa.jp/] was used for the simulations. Both benzene and cyclohexane were treated as a flexible six-center Lennard-Jones model (one of the United Atom (UA) models). The molecular models of benzene and cyclohexane applied to the UA model are also shown in **Figure 1**. The UA model assigns the CH and CH_2 groups into single interaction sites. The potential energy function is represented by the following equation accounting for the harmonic type of bonding potential, the theta type of angle potential, the cosine polynomial type of torsion potential and the Lennard-Jones (12-6) potential function for non-bonding interaction. The potential function used for all sites in the simulation is given as Eq. (1).

$$U(r^N) = \sum_{\text{Bond}}^{N} \frac{k_l}{2}(l-l_0)^2 + \sum_{\text{Angle}}^{N} \frac{k_\theta}{2}(\theta-\theta_0)^2 + \sum_{\text{Torsion}}^{N} a_k \cos^k(\phi) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\left[4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\}\right] \quad (1)$$

Here, k_l and k_θ are the spring constant of the bond length and bond angle, ε is the energy parameter, σ is the size parameter, r is the distance, and i and j denote the sites i and j, respectively.

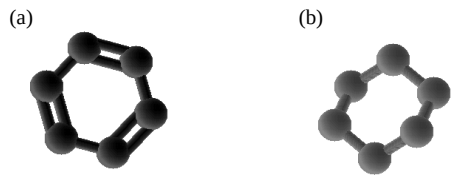

Fig. 1 Molecular structures of (a) benzene and (b) cyclohexane represented by united atom model

1.2 Parameters

The new potential parameters were determined from the previously reported parameter sets (Siepmann *et al*., 1997; Errington and Panagiotopoulos, 1999; Wick *et al*., 2000). The parameters were proposed to perform the MD simulation as a flexible molecular model by the COGNAC engine. After the torsion parameters for cyclohexane were determined empirically to represent the slope of density against the temperature, the energy parameters for each site were adjusted to the densities of pure components. The new parameters presented in this work are shown in **Table 1**. While the parameters of cyclohexane are relatively close to the parameters for large cyclic alkanes (Lee *et al.*, 2005) and small cyclic alkane (Rai *et al*., 2007), the density of cyclohexane could be represented well by the same size parameter.

The new parameters were applied to the simulation of the mixture. The Lorentz–Berthelot type combining rules were employed for the determination of the energy and size

parameters between different sites. Further, the concentration-dependent interaction parameter was introduced to improve the calculated results of mixtures density. The energy and size parameters between different sites were determined by the following equations.

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii} \times \varepsilon_{jj}} \tag{2}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{3}$$

The potential parameters and interaction parameters were determined by a trial-and-error method. The interaction parameter k_{ij} was represented as a function of benzene mole fraction.

Table 1 Potential parameters

	Benzene	Cyclohexane
Bond	CH-CH	CH_2-CH_2
Potential type	Harmonic	Harmonic
l_0 [nm]	0.140 *1	0.154 *2
k_l [kJ mol^{-1} nm^{-2}]	2.93×10^5 *3	2.93×10^5 *2
Angle	CH-CH-CH	CH_2-CH_2-CH_2
Potential type	Theta	Theta
θ_0 [rad] *4	1.047 *1	1.152 *2
k_θ [kJ mol^{-1} rad^{-2}]	523 *5	519 *2
Torsion	CH-CH-CH-CH	CH_2-CH_2-CH_2-CH_2
Potential type	Cosine	Cosine
k [kJ mol^{-1}]	10.0	10.0
N [-]	4	4
a_0 [-]	0.5722 *5	0.1771 *6
a_1 [-]	0.0718 *5	0.3542 *6
a_2 [-]	-0.0912 *5	0.0239 *6
a_3 [-]	-0.2346 *5	-0.5550 *6
Non-bond	CH-CH	CH_2-CH_2
Potential type	Lennard-Jones	Lennard-Jones
σ [nm]	0.3695 *1	0.3930 *2
ε [kJ mol^{-1}]	0.4875 *6	0.4480 *6
cut off [nm]	1.0	1.0

*1: Referred from Wick *et al.* (2000)
*2: Referred from Siepmann *et al.* (1997)
*3: Assumed to same as CH_2 groups
*4: External angle is used in COGNAC
*5: Referred from Errington and Panagiotopoulos (1999)
*6: Determined to experimental density of Sun *et al.* (1988)

1.3 Simulation conditions and analysis

In order to determine the simulation conditions, the simulation was performed on 108, 300 and 500 molecules and the parameters such as incremental time step, total time steps and cut-off length were changed by considering previous works and were determined not to influence the calculated results. As a result, the 300-molecule system was applied in this work. The boundary condition was set periodic and the initial positions of all molecules were assigned randomly avoiding the overlaps. The cut-off length was set to 1.0 nm and long range correction was applied. The incremental time step of the calculations was set at 1 fs. After 5×10^4 equilibration steps (50 ps) of the *NVT* ensemble MD and more than 5.0×10^5 equilibration steps (0.5 ns) of the *NPT* ensemble MD, more than three times 5×10^5 production steps (0.5 ns) were carried out. The temperature and pressure of this system were controlled by the Anderson method (1983). The legitimacy of simulation conditions and usage of parameters was confirmed by the *n*-butane system by comparing the simulated results of this work and the literature (Dysthe *at al.*, 2000). The simulations for each pure system were carried out at 283, 293, 298, 303 and 313 K. On the other hand, the simulation for mixture was performed only at 298 K, because the density and self-diffusion coefficients change linearly with temperature. The pressure of the systems was kept at atmospheric pressure (0.1 MPa). The density was calculated and averaged during the production steps by several simulations.

2. Results and Discussion

The densities of benzene and cyclohexane obtained through the simulation with the new parameters are shown in **Figure 2** as a function of temperature. The simulation results show good agreement with the experimental data for each pure component.

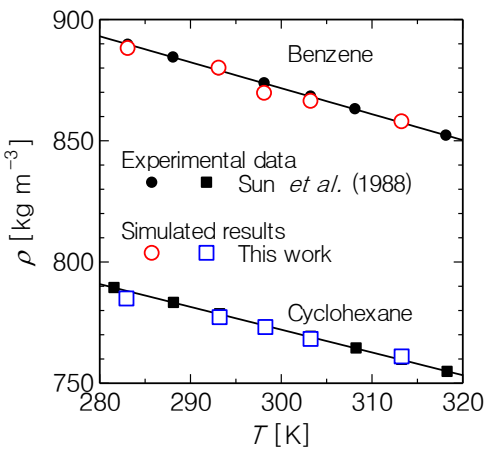

Fig. 2 Densities of benzene and cyclohexane as function of temperature at atmospheric pressure

The interaction parameters k_{12} were determined by the Adachi-Sugie type (1985) correlated function of Eq. (4). The Adachi-Sugie equation for the energy parameter, which was proposed for asymmetric systems, was adopted in the simulation presuming that the benzene+cyclohexane mixture was an asymmetric system of flat and distorted molecules. The

interaction parameter is a decreasing function of the mole fraction of benzene probably because interactions between the different sites (CH-CH_2) increase and those between the same sites (CH-CH) decrease with the mole fraction of benzene.

$$1-k_{12}=1.101-0.147(x_1-x_2)+0.108(x_1-x_2)^2-0.043(x_1-x_2)^3 \quad (4)$$

Here, x_1 and x_2 are the mole fraction of benzene and cyclohexane, respectively. The interaction parameter k_{12} is not defined for pure components (x_1=0 and 1).

The densities of benzene and cyclohexane mixture at 298 K, which were obtained by the present simulation, are shown in **Figure 3** together with the experimental data measured by Beg *et al.* (1994). Although the simulated results without the interaction parameter (i.e. k_{ij}=0) failed to express the experimental data at a benzene mole fraction smaller than 0.7, we are successful in representing the concentration dependence of density by introducing the concentration-dependent interaction parameter of Eq. (4).

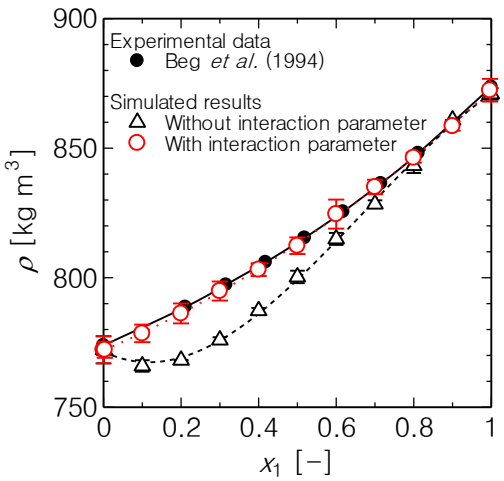

Fig. 3 Density as function of mole fraction for benzene(1) + cyclohexane(2) at 298 K and atmospheric pressure

The simulated self-diffusion coefficients of benzene and cyclohexane are shown in **Table 2** and **Figure 4**. Table 2 shows the calculated diffusion coefficients and the 90% confidence interval (C.I.). The self-diffusion coefficients were averaged by several simulations of different initial conditions and the confidence intervals were calculated by the averaged values and deviations. The confidence intervals are very small so that the calculated diffusion coefficients are reliable. The simulated self-diffusion coefficient of pure benzene was about 6% smaller than the experimental results. Diffusion in the direction normal to the flat plane of the benzene molecule would be suppressed, because the area of the flat plane of simulated molecular model would be larger than the real molecules. On the other hand, the simulated self-diffusion coefficient of pure cyclohexane was about 14% larger than the experimental data. This may be attributed to the size of molecules used in the present simulation, which should be somewhat smaller for representing the real molecules.

Table 2 Simulated results of self-diffusion coefficients for benzene (1) and cyclohexane (2) at 298 K and atmospheric pressure

Without interaction parameter (k_{ij}=0)

x_1 [-]	$D_1\times10^5$ [$cm^2\ s^{-1}$]	90 % C.I.	$D_2\times10^5$ [$cm^2\ s^{-1}$]	90 % C.I.
0.0			1.681	±0.072
0.0033	1.808	±0.032	1.617	±0.033
0.10	2.339	±0.054	2.153	±0.096
0.20	2.695	±0.023	2.442	±0.013
0.30	2.788	±0.116	2.514	±0.080
0.40	2.714	±0.014	2.497	±0.072
0.50	2.691	±0.134	2.519	±0.052
0.60	2.473	±0.092	2.249	±0.093
0.70	2.321	±0.061	2.095	±0.030
0.80	2.166	±0.067	2.032	±0.145
0.90	1.976	±0.058	1.771	±0.005
0.9967	2.061	±0.054	1.866	±0.179
1.0	2.109	±0.072		

With concentration-dependent interaction parameter

x_1 [-]	$D_1\times10^5$ [$cm^2\ s^{-1}$]	90 % C.I.	$D_2\times10^5$ [$cm^2\ s^{-1}$]	90 % C.I.
0.0			1.681	±0.060
0.0033	1.606	±0.036	1.639	±0.035
0.10	1.743	±0.021	1.831	±0.045
0.20	1.968	±0.085	1.882	±0.050
0.30	2.133	±0.059	1.996	±0.029
0.40	2.154	±0.066	1.962	±0.054
0.50	2.257	±0.093	2.050	±0.019
0.60	2.226	±0.058	2.050	±0.066
0.70	2.145	±0.043	1.919	±0.031
0.80	2.118	±0.060	1.918	±0.049
0.90	2.071	±0.061	1.855	±0.071
0.9967	2.054	±0.091	1.840	±0.137
1.0	2.109	±0.072		

Figure 4 shows the simulated self-diffusion coefficients in benzene and cyclohexane mixture at 298 K as a function of benzene mole fraction together with the experimental data measured by Milles (1965). The self-diffusion coefficients simulated without the concentration-dependent interaction parameter could not represent the experimental data, especially at a benzene mole fraction smaller than 0.7 because the simulated densities in this region were smaller than the experimental data, as shown in Figure 3. By including the concentration-dependent interaction parameter of Eq. (4), the agreement between the experimental data and the simulation

were very much improved for both benzene and cyclohexane. However, it may be observed in Figure 4 that the simulated benzene diffusivities are systematically lower than the experimental data. This might be attributed to the suppression of diffusion in the direction normal to the flat plane of benzene molecules, which was recognized in the simulation of the diffusivity of pure benzene.

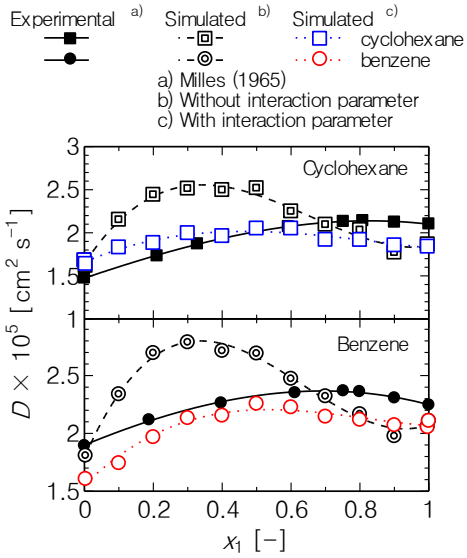

Fig. 4 Self-diffusion coefficient as function of benzene mole fraction for benzene (1) + cyclohexane (2) system at 298 K and atmospheric pressure

In our previous study (Higashi *et al.*, 2005), we found that the potential parameters and interaction parameter affect the diffusion coefficients (transport property) more severely than the solubility (equilibrium property). Some parameter sets which represented the solubility well could not represent the diffusion coefficients at all. This implies that the diffusion coefficient is more sensitive to the size parameter. In the present study, we found that the new potential parameters and interaction parameter were applicable for estimating the density (static property), but the quantitative estimation of diffusion coefficients (dynamic property) was not successful because the dynamic and transport properties are more sensitive to the size parameter.

Conclusion

New potential parameters have been proposed to calculate the density and the self-diffusion coefficients of a benzene and cyclohexane mixture by molecular dynamics simulation. The calculated densities of benzene, cyclohexane and their mixtures with the new potential parameters and the concentration-dependent interaction parameters were in good agreement with the experimental data. Further, the agreements between the experimental data and the simulated self-diffusion coefficients with the concentration-dependent interaction parameters were significantly improved for both benzene and cyclohexane in the mixture.

Nomenclature

a_i	= parameters of torsion potential	[-]
D	= diffusion coefficient	[m^2 s^{-1}]
k_l	= spring constant of bond length	[J mol^{-1} m^{-2}]
k_θ	= spring constant of bond angle	[J mol^{-1} rad^{-2}]
k_{ij}	= interaction parameter	[-]
l	= bond length	[m]
r	= distance between sites	[m]
U	= potential energy	[J]
x	= mole fraction	[-]
ε	= energy parameter	[J mol^{-1}]
ϕ	= torsion angle	[rad]
θ	= bond angle	[rad]
ρ	= density	[kg m^{-3}]
σ	= size parameter	[m]

<Subscripts>

1	= benzene
2	= cyclohexane
i, j	= sites

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