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Abstract

A molecular dynamics simulation was applied to carbon dioxide + trifluoromethylbenzoic acid isomer and carbon dioxide + methylbenzoic acid isomer systems to investigate the interactions between carbon dioxide and the solutes. The pair correlation functions between the carbon dioxide and trifluoromethyl group or methyl group in the solutes were calculated to study the fluorination effect of solvation. As a result, it was found that the interactions between carbon dioxide and trifluoromethyl group in trifluoromethylbenzoic acid isomers were stronger than those between carbon dioxide and the methyl group in methylbenzoic acid isomers. The simulation results had the same tendency as the experimental solubility enhancements and coincided with the trend of the interaction parameters of the Peng-Robinson equation of state that were determined from the solubility data.

Keywords : molecular simulation, interaction, fluorination effect, trifluorobenzoic acid, supercritical carbon dioxide

ACS Classification :

INTRODUCTION

Molecular simulation is one of the efficient methods to investigate the interactions of molecules in supercritical fluids. An ab initio calculation was applied and the favourable interaction between carbon dioxide and the polar fluoromethyl group of trifluoroethane and of trifluoropropane was indicated by Fried and Hu [1]. They also suggested that quadrupole-dipole interaction is an important contribution to the total energy of interaction. Galand and Wipff [2] performed molecular dynamics simulations and investigated the interaction between carbon dioxide and benzene derivatives. They concluded that the enhancement of the carbon dioxide-philicity upon fluorination does not stem from the enhanced individual interaction of the fluorinated group and the carbon dioxide molecule, but from the higher coordination number due to the increase of solvent accessible surface.

While the experimental enhancement for solubilities of solutes in supercritical carbon dioxide by fluorination of the solutes has been reported by several papers [3-7], the interaction between carbon dioxide and fluorinated compounds and the reason of the solubility enhancement remains controversial [8, 9]. An IR spectroscopic study [10] and a NMR study [11] revealed specific interactions were not the source of enhanced interaction. However, specific interactions between carbon dioxide and fluorine were shown to exist in another NMR study [12].

In a previous work [13], the authors measured the solubilities of 2-, 3- and 4-trifluoromethylbenzoic acids in supercritical carbon dioxide at 308.2, 313.2 and 323.2 K up to 22.6 MPa and compared those with non-fluorinated compounds. Solubility enhancements by fluorination were observed in the experimental results. The adjusted interaction parameters used in Peng-Robinson equation of state (PR-EOS), which was adopted to correlate the solubility data, indicated that the interaction between carbon dioxide and 4-trifluoromethylbenzoic acid is stronger than those between carbon dioxide and the other isomers. In this work, the interactions between carbon dioxide and solutes are discussed in terms of molecular simulation results. Although the partial molar volume, free volume, solvent-solvent or solute-solute interaction and some other variables are efficient to discuss the interaction in supercritical fluids, in this work, we have chosen to examine the solute-solvent interactions. The pair correlation functions and coordination numbers between solute and solvent were calculated. The pair correlation functions between carbon dioxide and trifluoromethyl group or methyl group in the solutes were used to investigate the fluorination effect on solvation of trifluoromethylbenzoic acid isomers in supercritical carbon dioxide. Further, the coordination number was calculated with the integration of the pair correlation function.

METHODS

Force Field

The simulation was performed by the Cerius^2 software (Molecular Simulation Inc.) and the Universal force field [14] contained in the software was mainly adopted for the simulation. Charged flexible models of all atom were adopted for carbon dioxide and solutes. To obtain non-bonded interactions, a Lennard-Jones 6-12 type expression by equation 1 was used for the van der Waals forces and electrostatic interactions were calculated by equation 2 in the Universal force field.

$$E_{\mathrm{vdw}} = D_0\left\{\left(\frac{R_0}{r}\right)^{12} - 2\left(\frac{R_0}{r}\right)^{6}\right\} \tag{1}$$

$$E_{\mathrm{el}} = E_0\left(\frac{q_i q_j}{\varepsilon\, r}\right) \tag{2}$$

where D_0 is the well depth, R_0 is the van der Waals bond length, E_0=1.39×10^{-3} J m mol^{-1}, q_i and q_j are the charges, r is the distance and ε is the relative dielectric constant.

The potential parameters and charge for all atom models of carbon dioxide are referred from the model by Harris and Yung [15]. These parameters were adjusted to represent vapor-liquid coexistence curve and critical properties of carbon dioxide. The parameters for atoms in the solute molecules were adopted from Universal force field [14] in the software. The charge for the atoms in the solute molecules was automatically assigned [16] by the software. The potential parameters of non-bonded interactions (van der Waals forces) for all atoms and charge for carbon dioxide are listed in **Table 1**. The molecular structures and partial charges for each solute are shown in **Figure 1**. The arithmetic and geometry combining rules were used to calculate the size and energy parameters between unlike molecules, respectively.

Simulation Conditions and Analysis

NVT ensemble molecular dynamics (MD) simulation was applied to calculate the pair correlation functions. A cubic cell with periodic boundary condition consisting of 300 carbon dioxide molecules and 1 solute molecule was adopted and the cut-off distance was set to be a half-cell for short-range van der Waals interactions between each pair atoms. The Ewald summation method [17] was applied for calculation of long-range Coulomb interactions. The relative dielectric constant was set to unity for the Universal force field and no distance cut-off was used for long-range Coulomb interactions. Temperature scaling was performed to adjust the temperature. The time step of the calculations was 1 fs. After energy minimization, 1.0×10^4 steps (10 ps) of the equilibration MD steps and 1.0×10^5 steps (100 ps) of the production MD steps were performed . The temperature and density were set to 313.2 K and 600 kg m^{-3}, respectively. The pair correlation functions between carbon atom of carbon dioxide and carbon atom of trifluoromethyl group or methyl group in the solutes, those between carbon atom of carbon dioxide and carbon atom of carboxylic group, and those between carbon atom of carbon dioxide and carbon atom of benzene ring were calculated. The coordination numbers were calculated from the pair correlation functions from 0 to 0.6 nm.

RESULTS AND DISCUSSION

It is expected that the partial charge of molecules will differ from the atoms involved in the molecules. As shown in **Figure 1**, the partial charge of trifluoromethylbenxzoic acids and methylbenzoic acids are similar, except for the fluorinated methyl group and the methyl group. The interactions of carbon dioxide with the fluorinated methyl group and with the methyl group seem to be very important. Generally, as the interaction between carbon dioxide and solute increased, the peak height of the pair correlation function and the number of carbon dioxide molecules interacting with the solute increased.

The simulated results for pair correlation functions between carbon dioxide and fluorinated methyl group and those between carbon dioxide and methyl group are shown in **Figure 2**. The first peaks of pair correlation function between carbon dioxide and trifluoromethyl group in trifluoromethylbenzoic acid isomers were higher than those of pair correlation function between carbon dioxide and methyl group in non-fluorinated compounds. Furthermore, the increase in the first peak height between carbon dioxide and fluorinated methyl group were almost the same as that in the literature [11]. The results showed that the fluorinated methyl group was more carbon dioxide-philic than the methyl group, which should be due to the change of partial charge by fluorination. The peaks of pair correlation functions between carbon dioxide and fluorinated methyl group for 4-trifluoromethylbenzoic acid and those between carbon dioxide and methyl group for 4-methylbenzoic acids were higher than the peaks of pair correlation functions between carbon dioxide and fluorinated methyl groups for 2-trifluoromethylbenzoic acid and those between carbon dioxide and methyl group for 2-methylbenzoic acid, respectively. Thus, greater screening effects of the carboxyl group for 2-trifluoromethylbenzoic acid and 2-mehylbenzoic acid can be concluded. The pair correlation function between carbon dioxide and trifluoromethyl group for 4-trifluoromethylbenzoic acid was the highest. This indicates that the interaction between carbon dioxide and fluorinated methyl group in 4-trifluoromethylbenzoic acid was the strongest.

Simulation results for pair correlation functions between carbon dioxide and carboxyl group are also shown in **Figure 3.** While the peaks of pair correlation functions between carbon dioxide and carboxyl group were broad for fluorinated compounds, the heights of the pair correlation functions between carbon dioxide and carboxyl group for non-fluorinated compounds were almost the same as those between carbon dioxide and the methyl group. The peak of pair correlation functions between carbon dioxide and carboxyl group decreased by the fluorination. It is known that carboxyl groups are strongly associated and have high carbon dioxide-philicity. However, simulated results show the carboxyl group in fluorinated compounds have relatively small carbon dioxide-philicty and the carboxyl group in non-fluorinated compounds have relatively high carbon dioxide-philicty. The electrostatic interactions are important to discuss the interaction of carbon dioxide and fluorinated compounds. Simulation results for pair correlation functions between carbon dioxide and a benzene ring are shown in **Figure 4.** The pair correlation functions between carbon dioxide and the benzene ring in fluorinated compounds were slightly higher than those in non-fluorinated compounds.

The coordination numbers calculated from the pair correlation functions are listed in **Table 2.** The number of carbon dioxide molecules solvating the trifluoromethyl group was larger than that of carbon dioxide molecules solvating the non-fluorinated methyl group. The calculated coordination numbers indicated carbon dioxide interactions increased by the fluorination from the results for trifluoromethyl group and methyl group. As a result, carbon dioxide molecules aggregated around fluorinated methyl group.

Cubic equations of state are widely used to estimate the solubility in supercritical fluids. The interaction parameters in an equation of state reflect the interaction between carbon dioxide and solute. The simulation results were compared with the interaction parameters in the PR-EOS which were used in a previous work [13]. The PR-EOS, combining and mixing rules used in the previous work [13] is written as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{3}$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \ , \qquad a_{ij} = \left(1-k_{ij}\right)\sqrt{a_i a_j} \tag{4}$$

$$b = \sum_i y_i b_i \tag{5}$$

where a and b are the energy and size parameters that can be calculated with the critical properties P_C and T_C and acentric factor ω. k_{ij} is the interaction parameter between unlike molecules i and j. The interaction parameters of the PR-EOS for the solute and solvent were adjusted by using solubility data [13] and these are shown in **Table 2**. Although the PR-EOS is an empirical equation, the interaction parameter for solute and solvent, (1- k_{12}), indicates the strength of interaction between solute and solvent. The interaction parameter was related to the coordination number. The coordination number versus (1- k_{12}) is shown in **Figure 5**. The interaction parameters exhibited a quadratic trend in coordination number, which means that the coordination number increased as the interaction between carbon dioxide and solute slowly increased.

CONCLUSION

Molecular dynamics simulations were performed to investigate the effect of fluorination on the interactions between carbon dioxide and fluorinated and non-fluorinated solutes. It was shown that the electrostatic interaction is very important to discuss the fluorination effect on the interaction. The interaction parameters in the PR-EOS empirically show quadratic dependence in coordination number of carbon dioxide around the solute. The possibility of existence for specific interaction between carbon dioxide and fluorinated methyl group was indicated by the simulation results. The interactions seem to stem from the partial charge of the solute molecules that is remarkably changed by fluorination. The conclusions presented in this work are mainly based on partial charges.

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LIST OF SYMBOLS

a	energy parameter in PR-EOS, Pa m^6 mol^{-2}
b	size parameter in PR-EOS, m^3 mol^{-1}
D_0	well depth of potential function, J mol^{-1}
E_{vdw}	van der Waals interaction potential, J mol^{-1}
E_{el}	electric interaction potential, J mol^{-1}
E_0	constant (1.39×10^{-3}), J m mol^{-1}

g	pair correlation function, -
k_{ij}	intermolecular interaction parameter, -
N	running coordination number, -
q	charge, e
R_0	van der Waals bond length, m
r	distance, m
v	molar volume, m^3 mol^{-1}

Greek Letter

ε	relative dielectric constant, -

Subscripts

i, j	components i and j
CF3	in trifluoromethyl group
CH3	in methyl group
CO2	in carbon dioxide
COOH	in carboxyl group
CR	in benzene ring
1	solvent (carbon dioxide)
2	solute

REFERENCES

[1] J.R. Fried, N. Hu, "The molecular basis of CO_2 interaction with polymers containing fluorinated groups: computational chemistry of model compounds and molecular

simulation of poly [bis(2,2,2- trifluoroethoxy)phosphazene]", Polymer 44 (2003) 4363-4372.

[2] N. Galand, G. Wipff, "Solvation of benzene derivatives in SC-CO_2: a molecular dynamics study of fluorination effects", New J. Chem. 27 (2003) 1319-1325.

[3] K.E. Laintz, C.M. Wai, C.R. Yonker, R.D. Smith, "Solubility of fluorinated metal diethyldithiocarbamates in supercritical carbon dioxide", J. Supercrit. Fluids 4 (1991) 194-198.

[4] T.A. Hoefling, R.M. Enick, E.J. Beckman, "Microemulsions in near-critical and supercritical CO_2", J. Phys. Chem. 95 (1991) 7127-7129.

[5] A. Laitinen, O. Jauhiainen, O. Aaltonen, "Solubility of fluorinated pharmaceuticals in dense carbon dioxide", Org. Process Res. Dev. 4 (2000) 353-356.

[6] M.P. Krafft, J.G. Riess, "Highly fluorinated amphiphiles and colloidal systems, and their applications in the biomedical field. A contribution", Biochimie 80 (1998) 489-514.

[7] R. Enick, E. Beckman, A. Yazdi, V. Krukonis, H. Schonemann, J. Howell, "Phase behavior of CO_2-perfluoropolyether oil mixtures and CO_2- perfluoropolyether chelating agent mixtures", J. Supercrit. Fluids 13 (1998) 121-126.

[8] P. Raveendran, S.L. Wallen, "Exploring CO_2-philicity: Effects of stepwise fluorination", J. Phys. Chem. B 107 (2003) 1473-1477.

[9] J.E. Brady, P.W. Carr, "A study of solvatochromic linear energy relationships in a homologous series of n-alkanes and n-alkylnitriles", J. Phys. Chem. 89 (1985) 1813-1822.

[10] G.G. Yee, J.L. Fulton, R.D. Smith, "Fourier-transform infrared-spectroscopy of molecular-interactions of heptafluoro-1-butanol or 1-butanol in supercritical carbon dioxide and supercritical ethane", J. Phys. Chem. 96 (1992) 6172-6181.

[11] C.R. Yonker, "Solution dynamics of perfluorobenzene, benzene, and perdeuteriobenzene in carbon dioxide as a function of pressure and temperature", J. Phys. Chem. A 104 (2000) 685-691.

[12] A. Dardin, J.M. DeSimone, E.T. Samulski, "Fluorocarbons dissolved in supercritical carbon dioxide. NMR evidence for specific solute-solvent interactions", J. Phys. Chem. B 102 (1998) 1775-1780.

[13] H. Higashi, Y. Iwai, K. Miyazaki, Y. Ogino, M. Oki, Y. Arai, "Measurement and correlation of solubilities for trifluoromethylbenzoic acid isomers in supercritical carbon dioxide", J. Supercrit. Fluids 33 (2005) 15-20.

[14] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard, W.M. Skiff, "UFF, a full periodic-table force-field for molecular mechanics and molecular dynamics simulations", J. Am. Chem. Soc. 114 (1992) 10024-10035.

[15] J.G. Harris, K.H. Yung, "Carbon dioxides liquid-vapor coexistence curve and critical properties as predicted by a simple molecular-model", J. Phys. Chem. 99 (1995) 12021-12024.

[16] A.K. Rappe, W.A. Goddard, "Charge equilibration for molecular dynamics simulations", J. Phys. Chem. 95 (1991) 3358-3363.

[17] P. Ewald, "Die berechnung opticher und elektrostatischer gitterpotentiale", Ann. Phys. 64 (1921) 253-287.

Table 1 Potential parameters

		R_0 [nm]	D_0 [kJ mol^{-1}]	q [e]
Carbon dioxide				
	C	0.3095 [a)]	0.23 [a)]	0.6512 [a)]
	O	0.3404 [a)]	0.67 [a)]	- 0.3256 [a)]
Trifluoromethylbenzoic acid or Methylbenzoic acid				
	C	0.3851 [b)]	0.44 [b)]	*
	H	0.2886 [b)]	0.18 [b)]	*
	F	0.3364 [b)]	0.21 [b)]	*
	O	0.3500 [b)]	0.25 [b)]	*

a) Harris and Yung [14]

b) Universal force field [15]

* Shown in **Figure 1**

Table 2 Coordination numbers and energy parameters

	$N_{\mathrm{CF3\text{-}CO2}}$ [-] a)	$N_{\mathrm{COOH\text{-}CO2}}$ [-] a)	$N_{\mathrm{CR\text{-}CO2}}$ [-] a)	$N_{2\text{-}1}$ [-] b)	1- k_{12} [-] d)
2-trifluoromethylbenzoic acid	6.9	6.6	6.6	53.1	0.908
3-trifluoromethylbenzoic acid	7.1	6.9	6.8	54.8	0.948
4-trifluoromethylbenzoic acid	7.5	6.6	7.0	56.1	1.062
	$N_{\mathrm{CH3\text{-}CO2}}$ [-] a)	$N_{\mathrm{COOH\text{-}CO2}}$ [-] a)	$N_{\mathrm{CR\text{-}CO2}}$ [-] a)	$N_{2\text{-}1}$ [-] c)	1- k_{12} [-] d)
2-methylbenzoic acid	6.5	6.6	6.7	53.3	0.904
3-methylbenzoic acid	6.8	7.0	6.5	52.8	0.896
4-methylbenzoic acid	7.1	7.2	6.6	53.9	0.870

a) $N_{i-j} = 4\pi\rho_j \int_0^{0.6} r^2 g_{ij}(r) dr$

b) $N_{2\text{-}1} = N_{\mathrm{CF3\text{-}CO2}} + N_{\mathrm{COOH\text{-}CO2}} + 6N_{\mathrm{CR\text{-}CO2}}$

c) $N_{2\text{-}1} = N_{\mathrm{CH3\text{-}CO2}} + N_{\mathrm{COOH\text{-}CO2}} + 6N_{\mathrm{CR\text{-}CO2}}$

d) Higashi et al. [13]

Figure Captions

Figure 1 Structures and charges for solute molecules.

(a) 2-Trifluoromethylbenzoic acid (d) 2-Methylbenzoic acid

(b) 3-Trifluoromethylbenzoic acid (e) 3-Methylbenzoic acid

(c) 4-Trifluoromethylbenzoic acid (f) 4-Methylbenzoic acid

Figure 2 Pair correlation functions between carbon dioxide and carbon atom of trifluoromethyl group or methyl group in the solute at 313.2 K and 600 kg m^{-3}.

(a) 2-Trifluoromethylbenzoic acid (——) ; 3-Trifluoromethylbenzoic acid (– –) ; 4-Trifluoromethylbenzoic acid (······).

(b) 2-Methylbenzoic acid (——) ; 3-Methylbenzoic acid (– –) ; 4-Methylbenzoic acid (······).

Figure 3 Pair correlation functions between carbon atom of carbon dioxide and carbon atom of carboxyl group in the solutes at 313.2 K and 600 kg m^{-3}.

(a) 2-Trifluoromethylbenzoic acid (——) ; 3-Trifluoromethylbenzoic acid (– –) ; 4-Trifluoromethylbenzoic acid (······).

(b) 2-Methylbenzoic acid (——) ; 3-Methylbenzoic acid (– –) ; 4-Methylbenzoic acid (······).

Figure 4 Pair correlation functions between carbon atom of carbon dioxide and carbon atom of benzene ring in the solutes at 313.2 K and 600 kg m^{-3}.

(a) 2-Trifluoromethylbenzoic acid (——) ; 3-Trifluoromethylbenzoic acid (– –) ;
4-Trifluoromethylbenzoic acid (······).

(b) 2-Methylbenzoic acid (——) ; 3-Methylbenzoic acid (– –) ;
4-Methylbenzoic acid (······).

Figure 5 Relationship of coordination number and interaction parameter for solute and solvent..

Trifluoromethylbenzoic acid isomers (○) ; Methylbenzoic acid isomers (△) ;
Quadratic curve (——), (1- k_{12})=0.015559 N_{2-1}^{2} - 1.6403 N_{2-1} + 44.115.

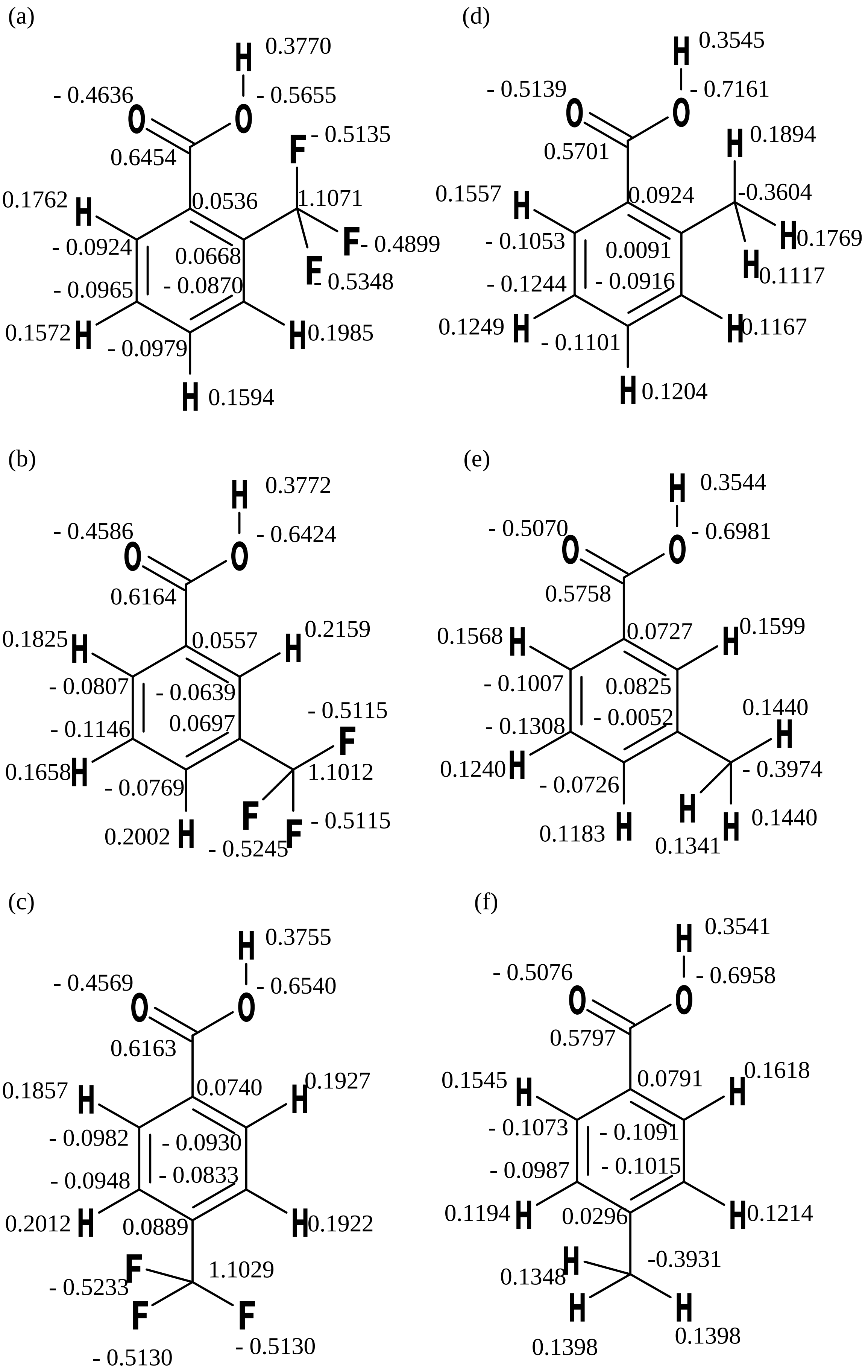

Fig.1 Higashi et al.

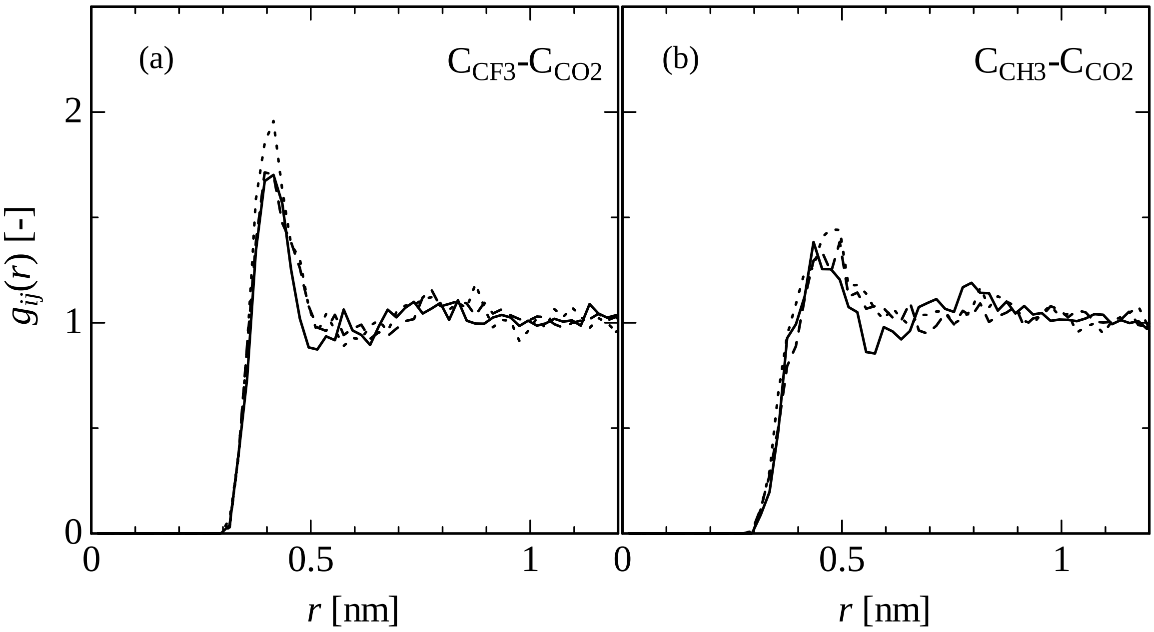

Fig.2 Higashi et al.

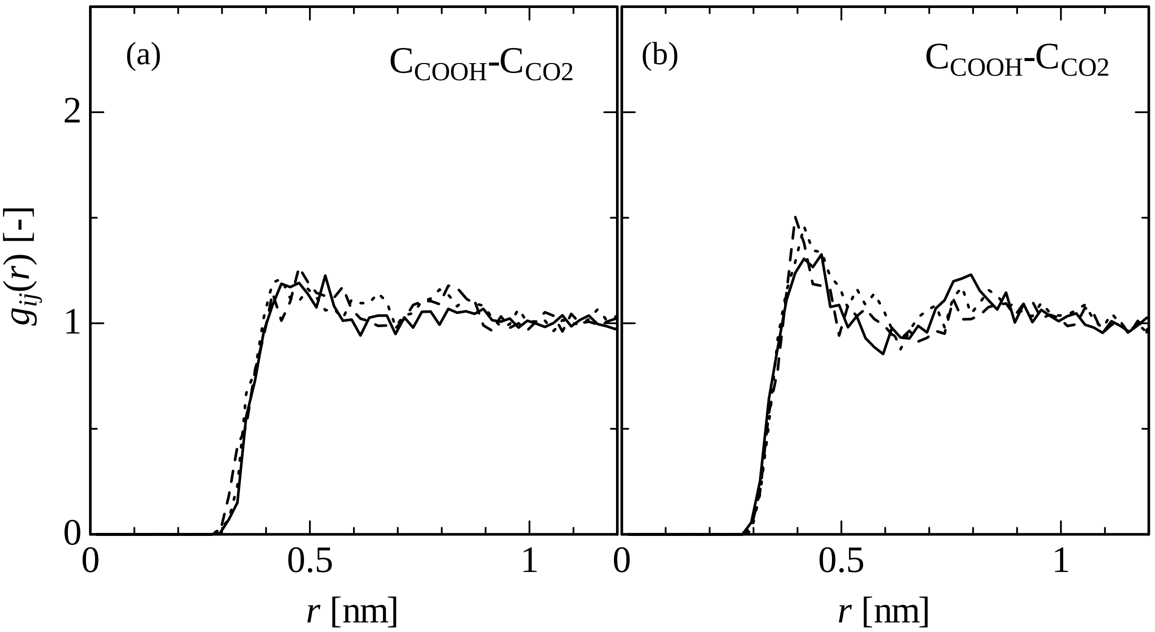

Fig.3 Higashi et al.

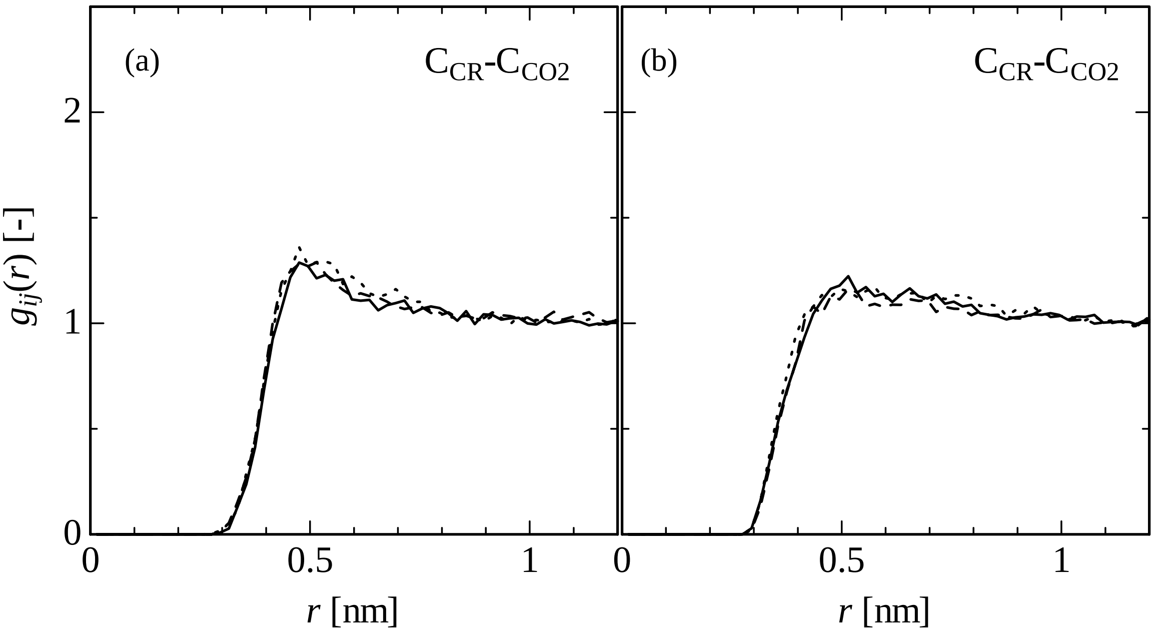

Fig.4 Higashi et al.

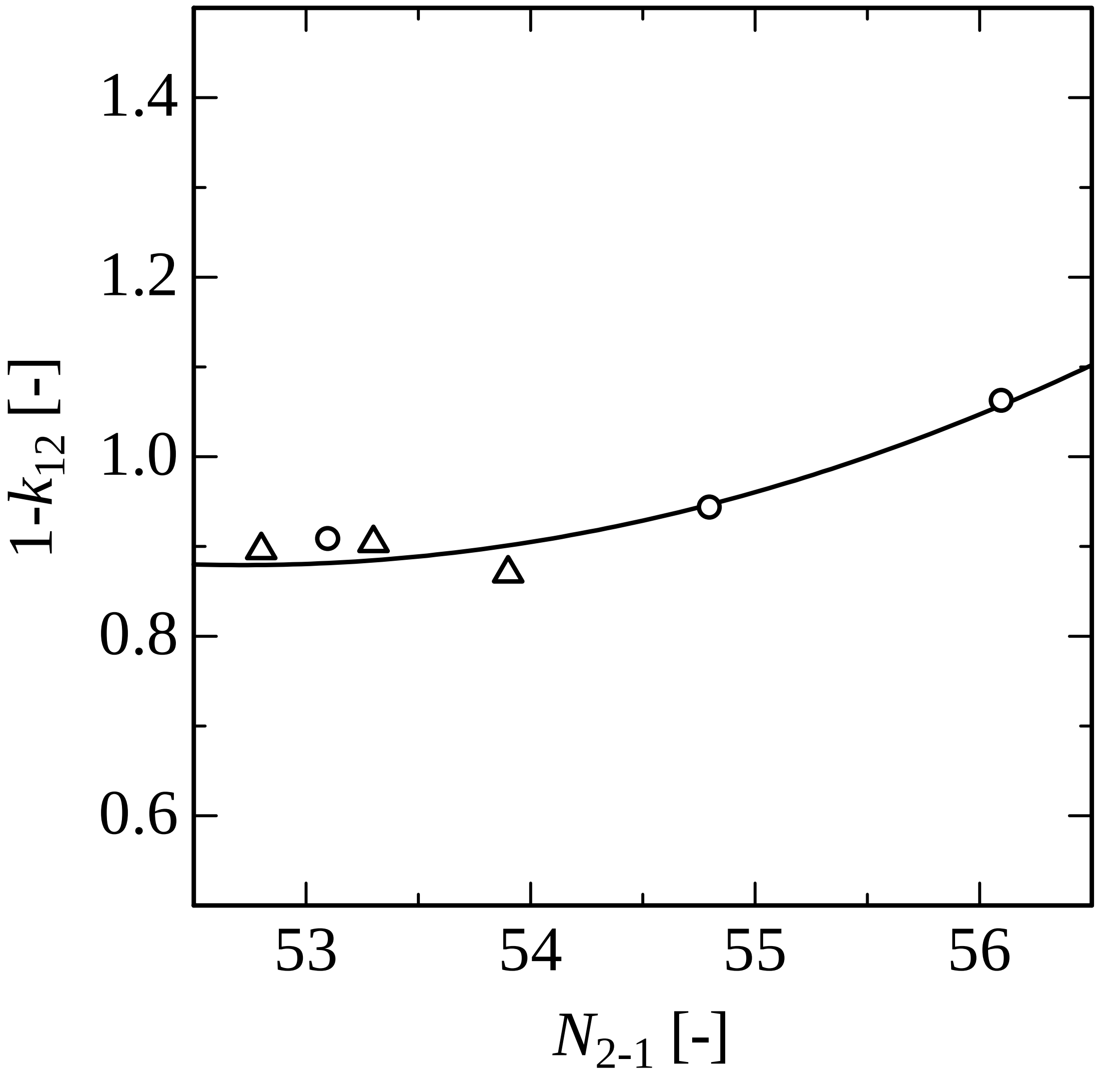

Fig.5 Higashi et al.