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Study of Self-Diffusion Coefficient in Nonassociating and Associating Fluids by a New Hard-Sphere Chain Equation

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The self-diffusion coefficient of non-associating fluids at moderate density and high density were calculated by the hard-sphere chain (HSC) equation obtained by the Chapman–Enskog method of solution which is corrected by molecular dynamics simulation data. Compared with the data of experiments or molecular simulations, the result shows that most of the average absolute deviation of the self-diffusion coefficient calculated by this method is about 5% when the pressure is lower than 300 MPa and the temperature is higher than 100 K. An attempt is made in this work to combine the hard-sphere chain model of the self-diffusion coefficient with the statistical associating fluid theory (SAFT). The real non-spherical associating molecules are modeled as chains of tangent hard-sphere segments with an associating site. An equation for the self-diffusion coefficient in polyatomic associating fluids is presented as a product of a non-hydrogen-bond contribution and a hydrogen-bond contribution. The SAFT equation provides the density and temperature dependence of an average number of hydrogen bonds in a molecule, and the HSC equation is used to calculate the self-diffusion coefficient for a non-associating fluid. The equation reproduces the experimental self-diffusion coefficient with an average absolute deviation of about 7.5% for water, alcohols and hydrogen fluoride over wide ranges of temperature and pressure, including supercritical water.

KEY WORDS: model; self-diffusion coefficient; hard-sphere chain equation; SAFT.

1. INTRODUCTION

The transport properties of liquids are very necessary in design calculations of chemical engineering. The self-diffusion coefficient of a gas at low densities

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may be calculated from the Enskog theory and its modification [1]. But there is not a well-founded self-diffusion theory for high density fluids. So often molecular dynamics (MD) simulations for simple spherical fluids, such as hard-sphere (HS) [2] fluids, have been employed to generate equations for the self-diffusion coefficient. In recent years, there has been much interest in understanding the dynamics of associating and non-associating chain molecular simulations.

We have recently developed a tangent hard-sphere chain (HSC) model [3] from the equation of self-diffusion in a HS fluid and molecular dynamics simulation data for a tangent HSC fluid. This allowed us to model a non-associating chain molecule as a chain of tangent hard-sphere segments and to obtain a new method for the correlation and prediction of the diffusion coefficient of non-associating chain molecules [4] over wide ranges of temperature and pressure.

An attempt is made in this work to use the HSC equation for associating chain molecules, so the HSC fluid theory is connected with the statistical associating fluid theory (SAFT). The statistical associating fluid theory [5–12] developed in recent years can be successfully used to calculate thermodynamic properties and phase equilibria for chain molecules, including associating fluids. In SAFT, the associating bond strength is quantified with a square-well potential. Each association site is assumed to have a different interaction with the various sites on another molecule. The mole fraction of molecules that are bonded can be obtained conveniently. In this work, real associating fluids are described as chains of flexible tangent hard-sphere segments with associating sites. The mole fraction of molecules that are bonded is calculated from the expression given in SAFT. The HSC model is extended to the case of an associating fluid, and an equation for the self-diffusion coefficient, in which the role of the associating bond is explicitly shown, is deduced. The equation is used to correlate the self-diffusion coefficients for water, alcohols and hydrogen fluoride over wide ranges of temperature and pressure.

2. BACKGROUND THEORY

2.1. Hard-Sphere Chain Model for the Self-Diffusion Coefficient

The self-diffusion coefficient for a dilute gas composed of hard spheres is given by

$$D_0 = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{1}$$

where ρ is the number density of a molecule. For dense gases, the well-known Enskog equation for a hard-sphere fluid is

$$D_{\mathrm{E}} = D_0/g(\sigma) = (3/8\rho\sigma^2)(kT/\pi m)^{1/2}\,[1/g(\sigma)] \tag{2}$$

where the radial distribution function at contact can be calculated from the Carnahan–Starling equation [13]

$$g(\sigma) = (1-0.5\eta)/(1-\eta)^3 \tag{3}$$

where

$$\eta = \pi\rho^*/6 = \pi\rho\sigma^3/6 \tag{4}$$

Comparing with molecular dynamics simulation data, Eq. (2) is valid only at low densities. In the moderate-density and high-density ranges, a correction factor has been obtained using the molecular dynamics simulation data by Ruckenstein and Liu [14]. Then the self-diffusion coefficient of a hard-sphere fluid can be expressed as

$$D_{\mathrm{HS}} = D_{\mathrm{E}}\, f(\rho^*) = D_0\, f(\rho^*)/g(\sigma) \tag{5}$$

where

$$f(\rho^*) = 1 + 0.94605\rho^{*1.5} + 1.4022\rho^{*3} - 5.6898\rho^{*5} + 2.6626\rho^{*7} \tag{6}$$

For a chain molecule containing N hard spheres of diameter σ and mass m, we assume its self-diffusion coefficient at the dilute gas condition is the same as that of a single hard sphere of diameter σ' and mass m' [15], i.e.,

$$D_{0C} = \frac{3}{8\rho\sigma'^2}\left(\frac{kT}{\pi m'}\right)^{1/2} \tag{7}$$

where σ' and m' can be calculated as

$$\sigma'^3 = N\sigma^3 \tag{8}$$

$$m' = Nm \tag{9}$$

which preserves the total volume and mass of molecules. From Eqs. (7)–(9), the following equation can be obtained

$$D_{0C} = \frac{3\sigma}{8\rho^* N^{1/6}}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{10}$$

Analogous to the self-diffusion coefficient equation for a hard-sphere fluid, the self-diffusion coefficient of a hard-sphere chain fluid can be expressed as:

$$D_{\mathrm{HSC}} = D_{0C} F(N, \rho^*)/g(\sigma') \tag{11}$$

where $g(\sigma')$ the radial distribution function at contact for the hard-sphere chain fluid, i.e.,

$$g(\sigma') = (1-0.5\eta')/(1-\eta')^3 \tag{12}$$

The volume fraction η is defined as

$$\eta' = \pi\rho^*/6 = \pi\rho N\sigma^3/6 \tag{13}$$

The correction function $F(N, \rho^*)$ in Eq. (11) can be obtained by using MD simulation results. Smith et al. [16] used equilibrium molecular dynamics to simulate fluids containing molecules modeled as chains of tangent hard spheres. We found the function $F(N, \rho^*)$ has the form

$$F(N, \rho^*) = \exp[-0.06356(N-1) - 0.05212\gamma\rho^* - 1.9709\gamma^2\rho^*] \tag{14}$$

where γ is $(N-1)/N$.

2.2. Effect of the Hydrogen Bond on the Self-Diffusion Coefficient

To explain the temperature dependence of the mass diffusion coefficient for glycerol-like liquids, Lishchuk and Malomuzh [17] employed the following reasons. To join to a weakly bound cluster, a molecule must first form with it at least one hydrogen bond. However, the formation of a hydrogen bond is connected with the escape rate across a potential barrier, separating the different states of a molecule [18],

$$D = D_{nh} \exp(-E_b/kT) \tag{15}$$

where D_{nh}, is a pre-factor and E_b is the relative barrier height. One can assume that the barrier height is proportional to the average number of hydrogen bonds formed by a molecule. Since the average number of hydrogen bonds increases when the temperature is lowered, the volume available for a displacement of a molecule should decrease [17]. In the present study, the barrier height is assumed to be proportional to the mole fraction of molecules bonded at association site A, i.e.,

$$E_b = C(1-X^{\mathrm{A}}) \tag{16}$$

where X^{A} is the mole fraction of molecules not bonded at association site A [5–12], and C is a constant for a given substance. For a non-associating fluid, $X^{\mathrm{A}}=1$ and $E_b=0$, $D_0=D_{nh}$. From Eq. (15), one can conclude that the pre-factor D_{nh} should be the self-diffusion coefficient for a non-associating fluid. Substituting Eq. (16) into Eq. (15), the following expression can be obtained

$$D=D_{nh}\exp[-c(1-X^{\mathrm{A}})/RT] \tag{17}$$

where $c=N_{\mathrm{A}}C$, and N_{A} is the Avogadro constant. An attempt to interpret the experimental self-diffusion coefficient data by means of Eq. (17) should then require knowledge of (i) the self-diffusion coefficient for a non-associating fluid, and (ii) the temperature and density dependence of the mole fraction of molecules not bonded at association site A. If real associating fluids are modeled as chains of flexible tangent HS segments with association sites, D_{nh} can be calculated from the HSC model for the self-diffusion coefficient, and the mole fraction of molecules not bonded at association site A can be obtained from the SAFT equation.

2.3. Mole Fraction of Molecules not Bonded at Association Site A

Hydrogen bonding is of short range and is a highly orientation-dependent site–site interaction. In the SAFT, the strength of association is modeled with a square-well potential and characterized by two parameters. The association sites on a single molecule are labeled with capital letters, A, B, C, etc. Each association site is assumed to have a different interaction with the various sites on another molecule. The mole fraction of molecules not bonded at site A can be determined as follows [5],

$$X^{\mathrm{A}}=1\bigg/\left(1+\sum_{\mathrm{B}}\rho X^{\mathrm{B}}\,\Delta^{\mathrm{AB}}\right) \tag{18}$$

where Δ^{AB} is the association strength. It is defined as

$$\Delta^{\mathrm{AB}}=4\pi F^{\mathrm{AB}}\int_d^{r_C} r^2\Omega(r)\,g(r)\,dr \tag{19}$$

where $4\pi r^2\Omega(r)\,dr$ is the bonding-site overlap volume element and F^{AB} is given by

$$F^{\mathrm{AB}}=\exp(\varepsilon^{\mathrm{AB}}/kT)-1 \tag{20}$$

The integral in Eq. (19) can be approximated as follows [8],

$$\Delta^{\mathrm{AB}} = g(d)\left[\exp\frac{\varepsilon^{\mathrm{AB}}}{kT} - 1\right] d^3 k^{\mathrm{AB}} \tag{21}$$

The association strength given by Eq. (21) depends on two parameters characterizing the association energy and volume, $\varepsilon^{\mathrm{AB}}$ and k^{AB}.

The expression for X^{A} obtained from Eq. (18) is dependent on the type of bonding in real associating fluids. The types of association bonding in water, alkanols and amines have been given by Huang and Radosz [6]. The various expressions for X^{A} corresponding to the type of bonding have been also tabulated in their paper [6]. In this work, type 4C is adopted for water. If two of the four sites in a water molecule are labeled O, representing the lone pair electrons of the oxygen atom, while the two others are labeled H to represent the hydrogen atoms, the O–H bonding strength is $\Delta^{\mathrm{OH}} = \Delta^{\mathrm{HB}} = \Delta$, while $\Delta^{\mathrm{OO}} = \Delta^{\mathrm{HH}} = 0$. This is because the O sites can bond to the H site only. The mole fraction of molecules not bonded at site A for water can be obtained from Eq. (18), i.e.,

$$X^{\mathrm{A}} = \frac{-1 + (1 + 8\rho\Delta)^{1/2}}{4\rho\Delta} \tag{22}$$

where Δ is the association strength,

$$\Delta = g(d)\left[\exp\left(\frac{\varepsilon^{\mathrm{HB}}}{kT}\right) - 1\right] d^3 k^{\mathrm{HB}} \tag{23}$$

For HF and alcohols, the type of hydrogen bonding is adopted to be 2B, and X^{A} is given by [6]

$$X^{\mathrm{A}} = \frac{-1 + (1 + 4\rho\Delta)^{1/2}}{2\rho\Delta} \tag{24}$$

3. RESULTS AND DISCUSSION

3.1. Results for Non-Associating Compounds

The self-diffusion coefficient of real non-associating fluids at high densities was calculated from the hard-sphere chain equation. The hard-sphere chain model outlined above was tested on *n*-alkanes from CH_4 to

Table I. Data for the Self-diffusion of the Compounds Studied in This Work

No.	Component	T (K)	M	P (MPa)	NDP*	Ref.
1	Methane	110.0–454.0	16.043	1.5–221.6	104	19
2	Ethane	136.0–454.0	30.070	25.–200.0	65	20
3	Propane	112.0–453.0	44.094	Sat.–200.0	95	20
4	*n*-Hexane	223.2–333.2	86.178	0.1–393.8	59	21
5	*n*-Heptane	185.6–371.2	100.206	3.1	11	22
6	*n*-Octane	248.2–348.1	114.232	0.1–360.8	43	22
7	*n*-Nonane	222.1–422.0	128.259	3.1	11	22
8	*n*-Decane	247.9–440.2	142.286	3.1	11	22
9	*n*-$C_{12}H_{26}$	264.2–434.8	170.340	3.1	11	22
10	*n*-$C_{30}H_{62}$	356.5–469.0	422.822	0.1–300	43	23
11	*n*-$C_{78}H_{158}$	403.0–473.0	1096.113	0.1–300	36	24
12	*n*-$C_{154}H_{310}$	412.0–473.0	2162.155	0.1–300	18	24
13	Chloromethane	186.0–440.0	50.488	Sat.–200	42	25
14	Dichloromethane	186.0–406.0	84.933	Sat.–200	43	25
15	Carbon disulfide	268.2–313.2	76.131	0.1–300	29	26
16	Carbon dioxide	223.0–450.0	44.011	1.0–200	105	27, 28

$C_{154}H_{310}$ and other organic substances. Table I lists the *n*-alkanes considered, the number of data points (NDP), and the temperature T and pressure P ranges involved. Densities of methane, ethane, and propane were calculated from equations proposed by Younglove and Ely [29], densities of *n*-heptane and higher *n*-alkanes from the Hudlestone equation [30], and other densities from the same references as the self-diffusion coefficients.

The resulting parameters along with the average absolute deviations (AAD) in the self-diffusion coefficient are listed in Table II. The AAD in Table Il is defined as

$$\mathrm{AAD} = \left(\sum_{i=1}^{\mathrm{NDP}} |(D_i^{\mathrm{CAL}} - D_i^{\mathrm{EXP}})/D_i^{\mathrm{EXP}}| \right) \Big/ \mathrm{NDP} \tag{25}$$

As seen from Table II, Eq. (11) provided accurate correlations for almost all the substances studied in this work. For most compounds, the AAD is comparable to the experimental uncertainly. The AAD for 16 substances is about 5%.

In Fig. 1, the self-diffusion coefficients for carbon disulfide at different temperatures are plotted against pressure. As seen from Fig. 1, the HSC equation gives good results. But when the pressure becomes high, the HSC equation yields higher values compared with the experimental values.

Table II. Parameters of the HSC Equation and the Average Absolute Deviations from the HSC Equation

No.	Component	N	$\sigma(10^{-10}\ \mathrm{m})$	AAD (%)
1	Methane	3.091	3.540	6.5
2	Ethane	3.551	4.544	6.1
3	Propane	2.576	3.431	7.1
4	*n*-Hexane	2.521	4.434	7.9
5	*n*-Heptane	2.083	4.711	7.8
6	*n*-Octane	2.117	4.915	6.3
7	*n*-Nonane	2.145	5.082	6.2
8	*n*-Decane	2.167	5.243	5.7
9	n-$C_{12}H_{26}$	2.281	5.472	5.9
10	n-$C_{30}H_{62}$	9.812	4.901	11.2
11	n-$C_{78}H_{158}$	26.774	5.012	8.7
12	n-$C_{154}H_{310}$	48.897	5.637	5.4
13	Chloromethane	2.718	4.102	2.9
14	Dichloromethane	2.901	5.469	3.2
15	Carbon disulfide	2.310	3.200	4.1
16	Carbon dioxide	1.001	3.551	3.9

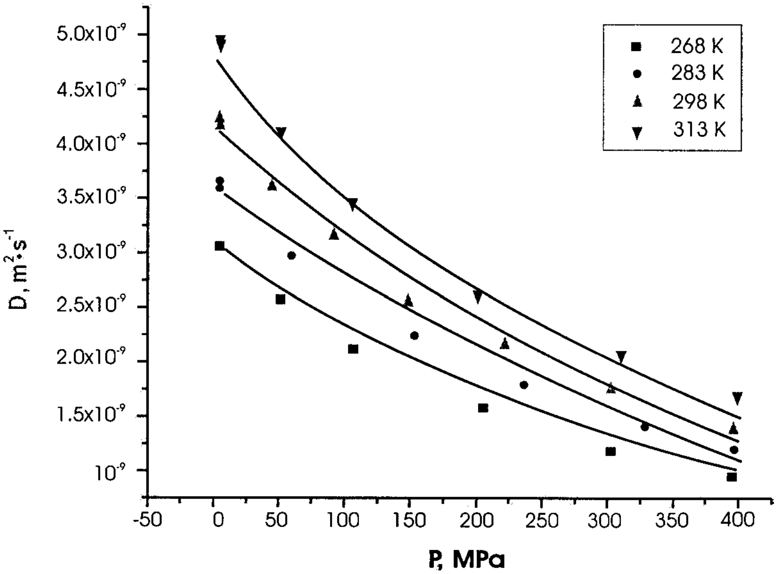

Fig. 1. Self-diffusion as a function of temperature and pressure for carbon disulfide. Solid line refers to the result of the HSC.

3.2. Results for Associating Compounds

Because water and hydrogen fluoride are near-spherical molecules, the values of the chain length N are set to be 1, the present self-diffusion coefficient equation has three adjustable parameters (σ, $\varepsilon^{\mathrm{HB}}$ and k^{HB}) for water and hydrogen fluoride, and four adjustable parameters (σ, N, $\varepsilon^{\mathrm{HB}}$ and k^{HB}) for other non-spherical associating substances. The values of these parameters are very different in the different published articles [31]. Therefore, they were determined from the experimental self-diffusion coefficient data with a Marquardt algorithm. Self-diffusion coefficient data for 10 typical real associating substances have been used to test Eq. (17) in the present work. The data sources, the numbers of data points, the temperature and pressure ranges of the self-diffusion coefficient for these associating substances studied are listed in Table III. The substances studied include water, alcohols and hydrogen fluoride. They are typical hydrogen-bonded liquids. They were chosen only when the self-diffusion coefficients at different temperatures and pressures are available. Mills [32] and Krynicki et al. [33] gave the temperature and pressure dependence of self-diffusion in water, and the densities are not available in their publications. In this case, the density of water under pressure was obtained from Vargaftik's tabulation [35] of the density at saturated vapor pressure and from Grindley and Lind [34] for the compressed liquid. If the density data are not available from the same reference as the self-diffusion coefficient (methanol and

Table III. Data for the Self-Diffusion of Compounds Studied in This Work

No.	Compounds	Formula	M	NDP	T (K)	P (MPa)	Reference
1	Water	H_2O	18.015	166	273.2–973.2	0.1–303.2	32, 33, 40–42[a]
2	Heavy water	D_2O	20.000	63	283.2–473.2	0.1–304.3	43
3	Oxygen-18 water	$H_2{}^{18}O$	20.016	37	277.2–333.2	0.1–304.3	40
4	Methanol	CH_4O	32.042	96	187.0–453.0	0.1–385.8	42, 44, 45[b]
5	Ethanol	C_2H_6O	46.069	139	173.0–437.0	0.1–250.0	42, 44, 46[b]
6	1-Propanol	C_3H_8O	60.096	53	287.8–317.8	0.1–400.0	46
7	2-Propanol	C_3H_8O	60.096	44	253.0–478.0	50–200.0	47[c]
8	1-Pentanol	$C_5H_{12}O$	88.150	85	206.6–468.6	50–200.0	48[d]
9	2-Pentanol	$C_5H_{12}O$	88.150	39	237.1–483.1	50–200.0	48[d]
10	HF	HF	20.006	20	243.9–374.1	50–300.0	49[e]

[a] Densities of water under high pressure were taken from Grindley and Lind [34].

[b] If the density data are not available from the same reference as the self-diffusion coefficient, they were calculated from Cibulka and Zikova [36].

[c] Densities were estimated from the Hankinson–Brobst–Thomson method [37].

[d] Densities were calculated from Wappmann et al. [38].

[e] Densities were calculated from the Tait equation with the parameters given in Ref. 39.

Table IV. Parameters of the Self-diffusion Coefficient and the Average Absolute Deviation for the Substances Studied in This Work

No.	Compound	N	σ (10^{-10} m)	$\varepsilon^{\mathrm{HB}}/k(K)$	k^{HB}	AAD (%)
1	Water	1.000	2.65	3674.52	5.798×10^{-6}	8.93
2	Heavy water	1.000	2.65	4028.92	5.798×10^{-6}	13.20
3	Oxygen-18 water	1.000	2.65	3653.46	5798×10^{-6}	6.94
4	Methanol	1.227	3.42	1080.42	3.142×10^{-2}	9.11
5	Ethanol	1.500	3.77	1560.63	1.095×10^{-2}	6.24
6	1-Propanol	2.110	3.77	2166.04	1.605×10^{-3}	2.31
7	2-Propanol	1.239	4.53	1141.20	6.032×10^{-2}	8.65
8	1-Pentanol	2.816	4.12	2006.27	1.379×10^{-3}	4.78
9	2-Pentanol	2.712	4.18	3296.03	1.065×10^{-5}	8.67
10	HF	1.000	2.46	1068.30	3.861×10^{-2}	4.59

ethanol), they were obtained from the Tait equation of Cibulka and Zikova [36].

It is known from spectroscopy that the association energy is different in H_2O, D_2O and H_2O^{18}. For heavy water and oxygen-18 water, the HS segment diameter, the segment–segment interaction energy, and the association volume parameters are regarded as the same as normal water.

The resulting parameters along with the average absolute deviations (AAD) in the self-diffusion coefficient are listed in Table IV. As seen from Table IV, the present self-diffusion coefficient equation provides accurate correlations for all the substances studied in this work. For most compounds, the AAD is comparable to the experimental uncertainty. The total AAD for the 10 substances is 7.5%. The logarithms of the self-diffusion coefficient as a function of temperature and pressure for liquid HF are shown in Fig. 2. The present self-diffusion coefficient equation gives excellent correlation results in the overall range considered, as one can see from Fig. 2.

4. CONCLUSION

The self-diffusion coefficient of real non-associating fluids at high densities was calculated with the hard-sphere chain equation and compared with data from experiments or molecular simulations. The results show that most of the average absolute deviations (AAD) of the self-diffusion coefficient calculated by this method are less than 5% when the pressure is lower than 300 MPa and the temperature is higher than 100 K. The

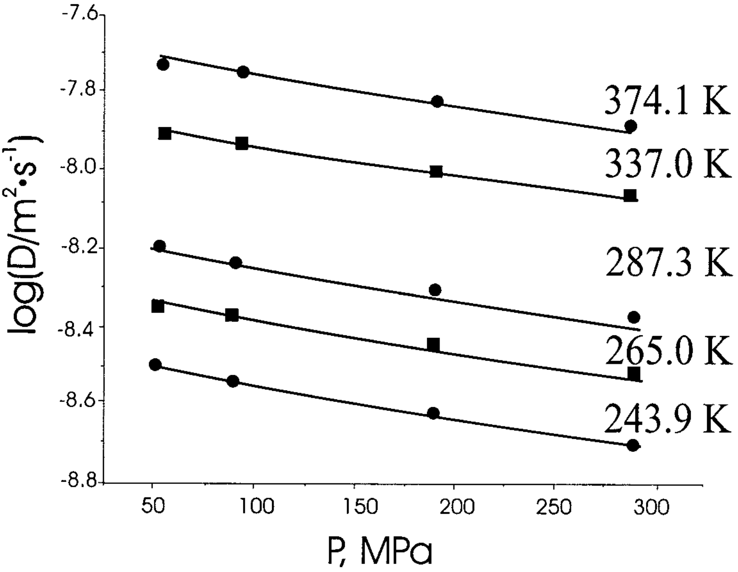

Fig. 2. The logarithm of the self-diffusion coefficient for liquid hydrogen fluoride as a function of temperature and pressure.

method is simpler than other methods, so the method can be used conveniently in calculation for chemical engineering applications.

In this work, an equation for the self-diffusion coefficient of an associating hard-sphere chain fluid was proposed by using the statistical associating fluid theory. In the equation, the role of the hydrogen bond is explicitly shown by the mole fraction of molecules not bonded at site A. The hard-sphere chain model was used to calculate the self-diffusion coefficient in the case of no hydrogen bond. The real associating substances were modeled as chains of tangent hard-sphere segments with association sites. The proposed equation was used to calculate the self-diffusion coefficients for 10 associating substances over wide temperature and pressure ranges. The segment-segment interaction energy parameter was estimated from the viscosity correlation, and the other parameters were determined from the experimental diffusion data. The average absolute deviation is about 7.5% for the 10 associating substances studied in this work. These results show that the proposed equation can be used to calculate the self-diffusion coefficient for associating substances with good accuracy. The equation proposed in this work is adequate to represent the self-diffusion coefficients for an associating fluid. We will extend the equation to mixtures in future work to demonstrate its predictive ability.

REFERENCES

1. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley, New York, 1954).
2. J. H. Dymond, *J. Chem. Soc. Rev.* **14**:317 (1985).
3. Y.-X. Yu and G.-H. Gao, *Fluid Phase Equil.* **166**:111 (1999).
4. Y.-X. Yu and G.-H. Gao, *Int. J. Thermophys.* **21**:57 (2000).
5. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**:1709 (1990).
6. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **29**:2284 (1990).
7. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **30**:1994 (1991).
8. W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys.* **65**:1057 (1988).
9. M. S. Wertheim, *J. Chem. Phys.* **87**:7323 (1987).
10. Y.-X. Yu, J.-F. Lu, J.-S. Tong, and Y.-G. Li, *Fluid Phase Equil.* **102**:159 (1994).
11. H. Adidharma and M. Radosz, *Fluid Phase Equil.* **161**:1 (1999).
12. P. K. Jog, A. Garcia-Cuellar, and W. G. Chapman, *Fluid Phase Equil.* **158**:321 (1999).
13. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
14. E. Ruckenstein and H. Liu, *Ind. Eng. Chem. Res.* **36**:3927 (1997).
15. P. H. Salim and M. A. Trebble, *J. Chem. Soc. Faraday Trans.* **191**:245 (1995).
16. S. W. Smith, C. K. Hall, and B. D. Freeman, *J. Chem. Phys.* **102**:1057 (1995).
17. S. V. Lishchuk and N. P. Malomuzh, *Chem. Phys. Lett.* **309**:307 (1999).
18. P. Hanggi, *J. Stat. Phys.* **42**:105 (1986).
19. K. R. Harris and N. J. Trappeniers, *Physica A* **104**:262 (1980).
20. S. Wappmann, M. Has, and H. D. Lüdemann, *J. Chem. Phys.* **94**:5643 (1991).
21. K. R. Harris, *J. Chem. Soc. Faraday Trans.* **178**: 265 (1982).
22. H. Ertl and F. A. L. Dullien, *AIChE J.* **19**:1217 (1973).
23. T. Gross, J. Buchhauser, and H. D. Ludemann, *J. Chem. Phys.* **109**:4518 (1998).
24. A. Woolf, *J. Chem. Soc., Faraday Trans.* **178**:583 (1982).
25. F. X. Prielmeier and H. D. Ludemann, *Mol. Phys.* **58**:593 (1986).
26. L. A. Woolf, *J. Chem. Soc., Faraday Trans.* **178**:583 (1982).
27. T. Gross, J. Buchhauser, and H.-D. Ludemann, *J. Chem. Phys.* **109**:4518 (1998).
28. P. Etesse, J. A. Zega, and R. Kobayashi, *J. Chem. Phys.* **97**:2022 (1992).
29. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* **16**:577 (1987).
30. A. K. Doolittle and D. B. Doolittle, *AIChE J.* **6**:157 (1960).
31. Y. X. Yu and G. H. Gao, *Fluid Phase Equil.* **179**:165 (2001).
32. R. Mills, *J. Phys. Chem.* **77**:685 (1973).
33. K. Krynicki, C. D. Green, and D. W. Sawyer, *Faraday Discuss. Chem. Soc.* **66**:199 (1979).
34. T. Grindley and J. B. Lind, *J. Chem. Phys.* **54**:3983 (1971).
35. N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases* (Hemisphere, Washington, DC, 1975).
36. I. Cibulka and M. Zikova, *J. Chem. Eng. Data* **39**:876 (1994).
37. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th Ed. (McGraw–Hill, New York, 1987).
38. S. Wappmann, N. Karger, and H.-D. Ludemann, *J. Chem. Eng. Data* **40**:233 (1995).
39. N. Karger and H.-D. Lüdemann, *J. Chem. Phys.* **109**:3301 (1998).
40. K. R. Harris and L. A. Woolf, *J. Chem. Soc., Faraday Trans.* **176**:377 (1980).
41. W. J. Lamb, G. A. Hoffman, and J. Jonas, *J. Chem. Phys.* **74**:6875 (1981).
42. F. A. L. Dullien, *AIChE J.* **18**:62 (1972).
43. D. J. Wilbur, T. DeFries, and J. Jonas, *J. Chem. Phys.* **65**:1783 (1976).
44. N. Karger, T. Vardag, and H.-D. Lüdemann, *J. Chem. Phys.* **93**:3437 (1990).

45. R. L. Hurle, A. J. Easteal, and L. A. Woolf, *J. Chem. Soc., Faraday Trans.* **181**:769 (1985).
46. S. Meckl and M. D. Zeidler, *Mol. Phys.* **63**:85 (1988).
47. N. Shaker-Gaafar, N. Karger, S. Wappmann, and H.-D. Lüdemann, *Ber. Buhsenges. Phys. Chem.* **97**:805 (1993).
48. N. Karger, T. Vardag, N. Shakergaafar, and H.-D. Lüdemann, *J. Mol. Liq.* **64**:211 (1995).
49. N. Karger, T. Vardag, and H.-D. Lüdemann, *J. Chem. Phys.* **100**:8271 (1994).