

Study on self-diffusion in water, alcohols and hydrogen fluoride by the statistical associating fluid theory

Yang-Xin Yu, Guang-Hua Gao*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

An attempt is made in this work to combine the Lennard–Jones chain model (LJC) of self-diffusion coefficient with the statistical associating fluid theory (SAFT). The real non-spherical associating molecules are modeled as chains of tangent Lennard–Jones segments with association sites. An equation for the self-diffusion coefficient in a polyatomic associating fluid 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 LJC equation is used to calculate the self-diffusion coefficient for a non-associating fluid. The segment–segment interaction energy ε is obtained from the critical temperature for alcohols and hydrogen fluoride, and, the segment diameter σ , the chain length N (the number of segments), association energy ε^{HB} and volume κ^{HB} are determined from the experimental diffusion data. The equation reproduces the experimental self-diffusion coefficient with total average absolute deviation of 6.69% for water, 6% alcohols and hydrogen fluoride over wide ranges of temperature and pressure, including the super-critical water. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Self-diffusion coefficient; Lennard–Jones chain model; SAFT; Associating fluid; Water; Alcohol

1. Introduction

The self-diffusion coefficients for dense fluids are important quantities required in engineering design for production, mass transfer, and processing. For polyatomic non-polar molecular fluids composed of spherical molecules, the self-diffusion coefficient can be calculated successfully by the hard sphere (HS) [1], square-well and Lennard–Jones (LJ) [2] models. If the molecules are non-spherical but not too long, Chandler's rough hard sphere theory [3] can be used as a connection between real and simple model fluids. Recently, the Lennard–Jones chain (LJC) model [4] has been developed through analyzing the molecular dynamics simulation data of hard sphere chain fluids. This model can be directly used to correlate and

* Corresponding author. Tel.: +86-10-62782558; fax: +86-10-62770304.

E-mail address: gaogh@tsinghua.edu.cn (G.-H. Gao).

predict the self-diffusion coefficients for polyatomic non-associating fluids [5]. Unfortunately, all the models described above cannot give good results for an associating fluid, especially for water. From experimental data of alcohols, Shaker-Gaafar et al. [6] found that the interacting sphere model [7], which has been used with good success for the description of non-polar liquids, fails for the alcohols. This is because the strong temperature dependence of self-diffusion coefficient observed in the hydrogen bonded liquids can definitely not be accounted for by a LJ potential which by its nature permit a fairly weak temperature dependence only.

Molecular association profoundly affects phase behavior and transport properties of pure fluids and fluid mixtures. This is because such associating fluids are known to contain not only monomeric molecules but also relatively long-lived (typically 1–10³ ps) clusters [8]. Several researchers [9–11] have studied the effect of hydrogen bond on the self-diffusion coefficient in water. The appreciably higher values found experimentally from the self-diffusion coefficients in hot and super-critical water show that the water molecules are far from being hard spheres. The models that consider the collective movement of clusters of hydrogen-bond molecules appear to describe the diffusion data well [9]. Ricci et al. [10] explained the behavior of the self-diffusion coefficient of water, along the coexistence curve, in terms of local fluctuation of “percentage of broken H-bond” as derived from infra-red spectra data. Lamanna et al. [11] examined the self-diffusion coefficient of water in terms of the fractions of water molecules with i hydrogen bonds ($i = 0, 1, 2, 3$ and 4) as a function of the temperature up to 500 K. The fit of the self-diffusion data along the saturation line is remarkable. Since the parameters used by Lamanna et al. [11] were determined below 500 K, extension of their calculation to the super-critical region is not warranted. A new equation is required to represent the self-diffusion coefficient in such associating fluids over wide ranges of temperature and pressure.

The statistical associating fluid theory (SAFT) [8,12–18] developed in recent years can successfully used to calculate the 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. This is very important in the studies of the structure and dynamic properties for associating fluids.

In this work, the real compounds are described as chains of freely tangent Lennard–Jones segments with associating sites. The mole fraction of molecules that are bonded is calculated from the expression given in SAFT. The LJC model [4] is extended to the case of 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. Expression for the self-diffusion coefficient

2.1. Effect of hydrogen bond on self-diffusion coefficient

To explain the temperature dependence of the mass diffusion coefficient for glycerol like liquids, Lishchuk and Malocule [19] 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 [20]:

$$D = D_{\text{nh}} \exp\left(-\frac{E_{\text{b}}}{kT}\right) \quad (1)$$

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 [19]. 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.

$$E_{\text{b}} = C(1 - X^{\text{A}}) \quad (2)$$

where X^{A} is the mole fraction of molecules not bonded at association site A [8,12–18], and C is a constant for a given substance. For a non-associating fluid, $X^{\text{A}} = 1$ and $E_{\text{b}} = 0$. From Eq. (1) one can conclude that the pre-factor D_{nh} should be the self-diffusion coefficient for a non-associating fluid. Substituting Eq. (2) into Eq. (1), the following expression can be obtained:

$$D = D_{\text{nh}} \exp\left[-\frac{c(1 - X^{\text{A}})}{RT}\right] \quad (3)$$

where $c = N_{\text{A}}C$, N_{A} the Avogadro constant. An attempt to interpret the experimental self-diffusion coefficient data by means of Eq. (3) 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 the real associating fluids are modeled as chains of freely tangent LJ segments with association sites, D_{nh} can be calculated from LJC 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.

2.2. Lennard–Jones chain model for the self-diffusion coefficient

In the previous paper [4], the self-diffusion coefficient equation for a polyatomic non-associating fluid has been proposed based on the LJC model. The equation of the self-diffusion coefficient for a freely tangent LJC fluid can be expressed as

$$D_{\text{LJC}} = \frac{D_{0\text{C}}}{[\{g(d)/F(N, \rho^*)\} + 0.4/T^{*1.5}]} \quad (4)$$

where $D_{0\text{C}}$ is obtained through assuming that the self-diffusion coefficient of a chain molecule at dilute gas condition is the same as that of a single hard sphere molecule having the same volume and mass, i.e.

$$D_{0\text{C}} = \frac{3d}{8\rho^*N^{1/6}} \left(\frac{kT}{\pi m}\right)^{1/2} \quad (5)$$

In Eq. (4), the radial distribution function at contact, $g(d)$, is given by Carnahan and Starling [21]

$$g(d) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (6)$$

where $\eta = \pi\rho^*/6 = \pi\rho Nd^3/6$, ρ is the number density of a chain molecule, N the chain length expressed as the number of segments in a molecule, and d is the effective hard sphere diameter. The correction function $F(N, \rho^*)$ was obtained from the molecular dynamics simulation data for hard sphere and hard sphere chain (HSC) fluids [4]. It has the form

$$F(N, \rho^*) = f(\rho^*) \exp[-0.06356(N - 1) - 0.05212\gamma\rho^* - 1.9709\gamma^2\rho^*] \quad (7)$$

where $\gamma = (N - 1)/N$,

$$f(\rho^*) = 1 + 0.94605\rho^{*1.5} + 1.4022\rho^{*3} - 5.6898\rho^{*5} + 2.6626\rho^{*7} \quad (8)$$

T^* in Eq. (4) is the reduced temperature. It is defined as

$$T^* = \frac{kT}{\varepsilon} \quad (9)$$

where ε is the Lennard–Jones segment–segment interaction energy parameter.

There are various theoretical expressions for the effective hard sphere diameter. Ruckenstein and Liu [2] tested them using a large number of molecular dynamics simulation data and found that the Boltzmann effective hard sphere diameter with the parameters given by Ben-Amotz and Herschbach [22] leads to the best agreement with the diffusion data of a LJ fluid. This expression was adopted in our calculations.

$$d = 1.1532\sigma \left[1 + \left(\frac{T^*}{0.527} \right)^{1/2} \right]^{-1/6} \quad (10)$$

where σ is the LJ segment diameter.

2.3. Mole fraction of molecules not bonded at association site A

Hydrogen bonding is of short range and highly orientation-dependent site–site interactions. 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 [8]:

$$X^A = \frac{1}{1 + \sum_B \rho X^B \Delta^{AB}} \quad (11)$$

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

$$\Delta^{AB} = 4\pi F^{AB} \int_d^{r_c} r^2 \Omega(r) g(r) dr \quad (12)$$

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

$$F^{AB} = \exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1 \quad (13)$$

The integral in Eq. (12) can be approximated as follows [14]:

$$\Delta^{AB} = g(d) \left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1 \right] d^3 \kappa^{AB} \quad (14)$$

The association strength given by Eq. (14) depends on two parameters characterising the association energy and volume.

The expression for X^A obtained from Eq. (11) 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 [12]. The various expressions for X^A corresponding to the type of bonding have been also tabulated in their paper [12]. 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 labeled H represent the hydrogen atoms, the O–H bonding strength is $\Delta^{OH} = \Delta^{HB} = \Delta$ while $\Delta^{OO} = \Delta^{HH} = 0$. 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. (11), i.e.

$$X^A = \frac{-1 + (1 + 8\rho\Delta)^{1/2}}{4\rho\Delta} \quad (15)$$

where Δ is the association strength.

$$\Delta = g(d) \left[\exp\left(\frac{\varepsilon^{HB}}{kT}\right) - 1 \right] d^3 \kappa^{HB} \quad (16)$$

For HF and alcohols, the type of hydrogen bonding is adopted to be 2B, and X^A is given by [12]

$$X^A = \frac{-1 + (1 + 4\rho\Delta)^{1/2}}{2\rho\Delta} \quad (17)$$

3. Results and discussion

The self-diffusion coefficient equation developed above should be tested against molecular simulation data at first. Gonzalez et al. [23] performed molecular dynamics simulations with a polarizable model for ethanol. Although the structure and dynamics of the liquid ethanol at three experimental densities and at critical conditions were investigated, it is hard to use their data to test our model because the two models are different. Therefore, self-diffusion coefficient data for 10 typical real associating substances have been used to test Eq. (3) in present work. The data sources, the numbers of data points, the temperature and pressure ranges of the self-diffusion coefficients for 10 associating substances studied are listed in Table 1. 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 [27] and Krynicky et al. [28] 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 [30] of the density at saturated vapor pressure and the compressions of Grindley and Lind [29]. If the density data are not available from the same reference as the self-diffusion coefficient for methanol and ethanol, they were obtained from the Tait equation of Cibulka and Zikova [34]. The saturated liquid densities and the vapor pressures required

Table 1

Database of the self-diffusion coefficients for the compounds studied in this work

No.	Compounds	Formula	<i>M</i>	NDP	<i>T</i> (K)	<i>p</i> (MPa)	Data reference
1	Water	H ₂ O	18.015	166	273.2–973.2	0.1–303.2	[24–26], [27,28] ^a
2	Heavy water	D ₂ O	20.000	63	283.2–473.2	0.1–304.3	[31]
3	Oxygen-18 water	H ₂ ¹⁸ O	20.016	37	277.2–333.2	0.1–304.3	[24]
4	Methanol	CH ₄ O	32.042	96	187.0–453.0	0.1–385.8	[26,32,33] ^b
5	Ethanol	C ₂ H ₆ O	46.069	139	173.0–437.0	0.1–250.0	[26,32,37] ^b
6	1-Propanol	C ₃ H ₈ O	60.096	53	287.8–317.8	0.1–400.0	[37]
7	2-Propanol	C ₃ H ₈ O	60.096	44	253.0–478.0	50–200.0	[6] ^c
8	1-Pentanol	C ₅ H ₁₂ O	88.150	85	206.6–468.6	50–200.0	[39] ^d
9	2-Pentanol	C ₅ H ₁₂ O	88.15	39	237.1–483.1	50–200.0	[39] ^d
10	Hydrogen fluoride	HF	20.006	20	243.9–374.1	50–300.0	[41] ^e

^a Densities of water under high pressures were taken from Grindley and Lind [29], and the saturated densities and vapor pressures were taken from Vargaftik [30].

^b If the density data are not available from the same reference as the self-diffusion coefficient, they were calculated from Cibulka and Zikova [34], the saturated liquid densities were calculated from Cibulka [35], and the vapor pressures were obtained from Ambrose and Walton [36].

^c Densities were estimated from the Hankinson-Brobst–Thomson method [38].

^d Densities were calculated from Wappmann et al. [40].

^e Densities were calculated from Tait equation with the parameters given in [42].

in the Tait equation were calculated from Cibulka [35] and Ambrose and Walton [36], respectively. The density of 2-propanol was estimated from Hankinson-Brobst–Thomson method [38].

The present associating LJC model has six parameters σ , ε , N , c and the association energy ε^{HB} and volume κ^{HB} . As pointed by Ruckenstein and Liu [2], and Yu and Gao [4], the self-diffusion coefficient is much more sensitive to the segment diameter σ and the chain length N than to the segment energy parameter ε . The segment–segment interaction energy parameter should depend on the critical temperature in a simple manner. For water the segment–segment interaction energy parameter was taken from Reid et al. [38], i.e.

$$\frac{\varepsilon}{k} = 809.1 \text{ K} \quad (18)$$

This value of ε/k was determined from viscosity data of water. For other substances, the correlation obtained from viscosity data by Chung et al. [43] is employed. If the molecular energy is assumed to be the sum of all the LJ segment energies, one can obtain:

$$N \left(\frac{\varepsilon}{k} \right) = \frac{T_c}{1.2593} \quad (19)$$

where T_c is the critical temperature. The critical temperature used to calculate the energy parameter ε was taken from the compilation of Reid et al. [38] except for 2-pentanol. The critical temperature of 2-pentanol was obtained from Daubert and Danner [44] because it is not available from the compilation of Reid et al. [38]. By analyzing the self-diffusion coefficient data of the substances studied, we found that the constant c is only dependent on the chain length N . The value of the constant c can be approximated

by

$$c = 5303.8N^{1/2} \quad (20)$$

The other four parameters should depend on the molecular size and shape, and hydrogen bonding. Because water and hydrogen fluoride are near spherical molecules, the value of the chain length N was set to be 1.

The present model does not explicitly account for the effects of dipole–dipole interaction and polarizability, although these are believed to be important for associating fluids. We expect that adjustment of the parameters can partially correct for errors due to neglect of these effects in the theory.

In summary, the present self-diffusion coefficient equation has three adjustable parameters (σ , ε^{HB} and κ^{HB}) for water and hydrogen fluoride, and four adjustable parameters (σ , N , ε^{HB} and κ^{HB}) for other non-spherical associating substances. The values of these parameters are very different from the different published articles. Therefore, they were determined from the experimental self-diffusion coefficient data with a Marquardt algorithm. The objective function (OF), simultaneously minimize the difference between the calculated and experimental self-diffusion coefficient data.

$$\text{OF} = \sum_{i=1}^{\text{NDP}} \left[\frac{D_i^{\text{cal}} - D_i^{\text{exp}}}{D_i^{\text{exp}}} \right]^2 \quad (21)$$

It is known from spectroscopy that association energy is different in H_2O , D_2O and H_2^{18}O . For heavy water and oxygen-18 water, the LJ segment diameter, the segment–segment interaction energy, and the association volume parameters are regarded as the same of normal water. Only one parameter ε^{HB} for heavy water and oxygen-18 water was determined from the experimental self-diffusion coefficient data.

The obtained parameters along with the average absolute deviations (AAD) in the self-diffusion coefficient are listed in Table 2. The AAD in Table 2 is defined as

$$\text{AAD} = \frac{1}{\text{NDP}} \sum_{i=1}^{\text{NDP}} \left| \frac{D_i^{\text{cal}} - D_i^{\text{exp}}}{D_i^{\text{exp}}} \right| \times 100\% \quad (22)$$

Table 2

The parameters of the self-diffusion coefficient equation and the average absolute deviations for the substances studied this work

No.	Compound	NDP	σ (nm)	$N\varepsilon/k$ (K)	N	$\varepsilon^{\text{HB}}/k$ (K)	κ^{HB}	AAD (%)
1	Water	166	0.2530	809.10	1.000	3674.52	5.798×10^{-6}	7.73
2	Heavy water	63	0.2530	809.10	1.000	4028.92	5.798×10^{-6}	12.18
3	Oxygen-18 water	37	0.2530	809.10	1.000	3653.46	5.798×10^{-6}	6.52
4	Methanol	96	0.3402	407.05	1.224	1080.42	3.142×10^{-2}	8.64
5	Ethanol	139	0.3765	408.08	1.454	1560.13	1.095×10^{-2}	5.62
6	1-Propanol	53	0.3764	426.27	2.002	2166.04	1.605×10^{-3}	1.79
7	2-Propanol	44	0.4499	403.64	1.230	1141.20	6.032×10^{-2}	8.28
8	1-Pentanol	85	0.3974	443.26	2.775	2006.27	1.379×10^{-3}	4.06
9	2-Pentanol	39	0.4083	438.34	2.658	3296.03	1.065×10^{-5}	8.10
10	HF	20	0.2360	366.08	1.000	1068.30	3.861×10^{-2}	4.02
Total		742						6.69

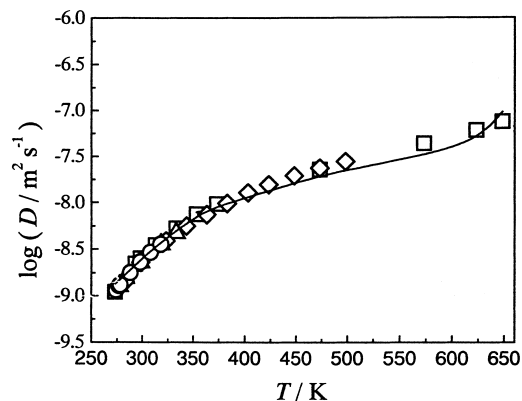


Fig. 1. The logarithms of the self-diffusion coefficient for water as a function of temperature along the saturated line. Solid line refers to the calculated values, symbols refer to the experimental data: (Δ) Harris and Woolf [24]; (\square) Dullien [26]; (\circ) Mills [27]; (\diamond) Krynicki et al. [28].

As seen from Table 2, The present self-diffusion coefficient equation provides accurate correlation for all the substances studied in this work. For most compounds, the AAD is comparable to the experimental uncertainty. The total AAD for 10 substances is 6.69%.

The self-diffusion coefficients for water at all states are correlated with one set of parameters, and the AAD is 7.73%. In Fig. 1, the logarithms of the self-diffusion coefficient for water, along the coexistence curve, are plotted against temperature from 273.15 K to the critical point. As one can see from Fig. 1, the agreement between the theoretical expression and the experimental data is very good except in the sub-critical region. The present equation underestimates the self-diffusion coefficient for water in the sub-critical region. The self-diffusion coefficients as a function of temperature and pressure for compressed liquid water and compressed super-critical water are shown in Figs. 2 and 3, respectively. As shown in these figures, the present equation can represent the self-diffusion coefficients for water at

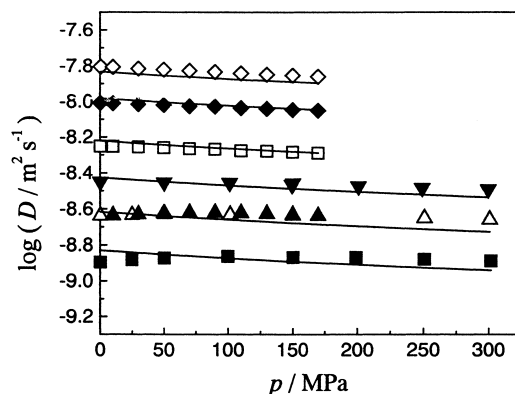


Fig. 2. The logarithms of the self-diffusion coefficient for compressed water as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data: (\blacksquare) 227.15 K [24]; (\triangle) 298.15 K [24]; (\blacktriangle) 298.2 K [28]; (\blacktriangledown) 318.15 K [24]; (\square) 343.2 K [28]; (\blacklozenge) 383.2 K [28]; (\diamond) 423.2 K [28].

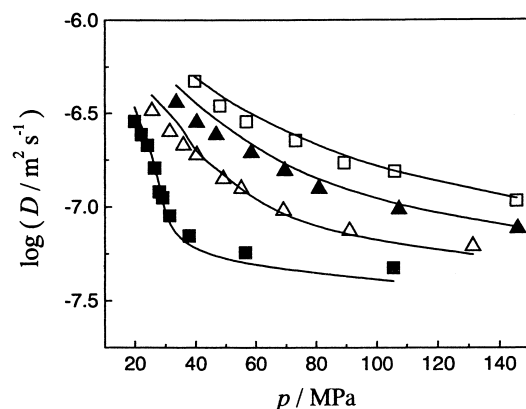


Fig. 3. The logarithms of the self-diffusion coefficient for compressed super-critical water as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data [25]: (■) 673.15 K; (△) 773.15 K; (▲) 873.15 K; (□) 973.15 K.

all states with good accuracy. Although the expressions derived by Ricci et al. [10] and Lamanna et al. [11] can be used to represent the self-diffusion coefficient for water very accurate along the saturation line, they are not suitable to water at other conditions, especially at super-critical region. Considering the wide ranges of temperature and pressure, the calculation results for water in this work are satisfactory.

The logarithms of the self-diffusion coefficient as a function of temperature and pressure for methanol, ethanol, 1-propanol, 2-propanol, 1-pentanol, 2-pentanol and liquid HF are shown in Figs. 4–10, respectively. The present self-diffusion coefficient equation gives excellent correlation results in the overall range considered, as one can see from Figs. 4–10. 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 the future work to demonstrate its predictive ability.

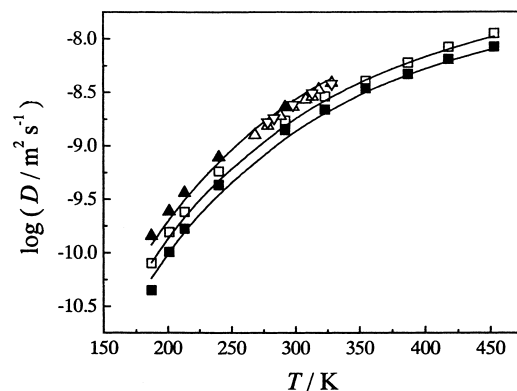


Fig. 4. The logarithms of the self-diffusion coefficient for methanol as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data: (△) 0.1 MPa [26]; (▲) 0.1 MPa [32]; (▽) 0.1 MPa [33]; (□) 100 MPa [32]; (■) 200 MPa [32].

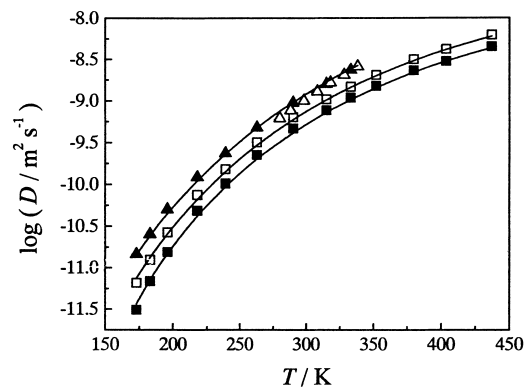


Fig. 5. The logarithms of the self-diffusion coefficient for ethanol as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data: (Δ) 0.1 MPa [26]; (\blacktriangle) 0.1 MPa [32]; (\square) 100 MPa [32]; (\blacksquare) 200 MPa [32].

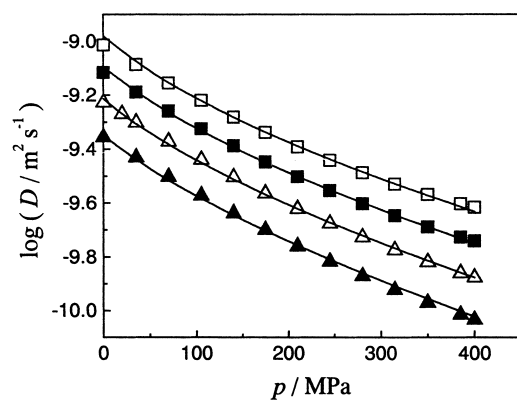


Fig. 6. The logarithms of the self-diffusion coefficient for 1-propanol as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data [37]: (\square) 317.8 K; (\blacksquare) 308.1 K; (Δ) 298.4 K; (\blacktriangle) 287.8 K.

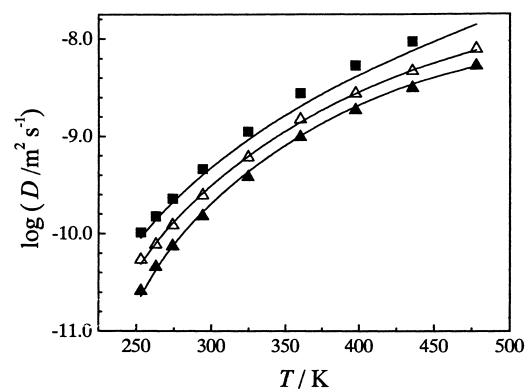


Fig. 7. The logarithms of the self-diffusion coefficient for 2-propanol as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data [6]: (\blacksquare) 5 MPa; (Δ) 100 MPa; (\blacktriangle) 200 MPa.

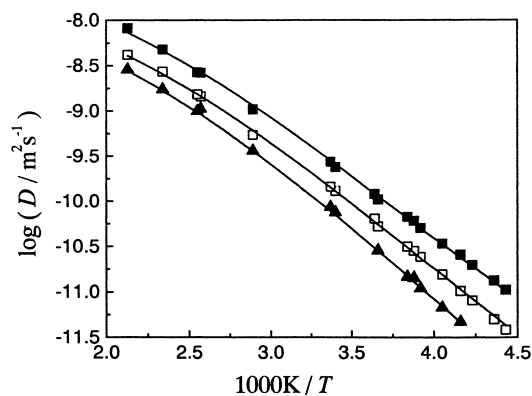


Fig. 8. Isobars of the self-diffusion coefficient for 1-pentanol. Solid lines refer to the calculated values, symbols refer to the experimental data [39]: (■) 5 MPa; (□) 100 MPa; (▲) 200 MPa.

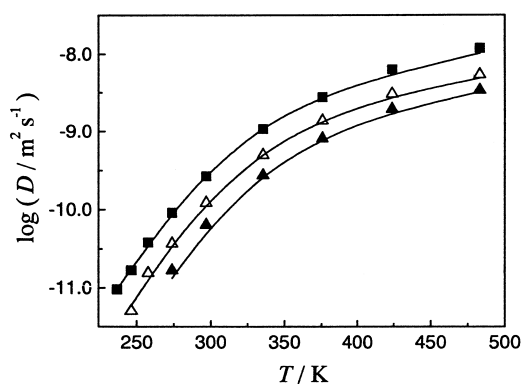


Fig. 9. The logarithms of the self-diffusion coefficient for 2-pentanol as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data [39]: (■) 5 MPa; (△) 100 MPa; (▲) 200 MPa.

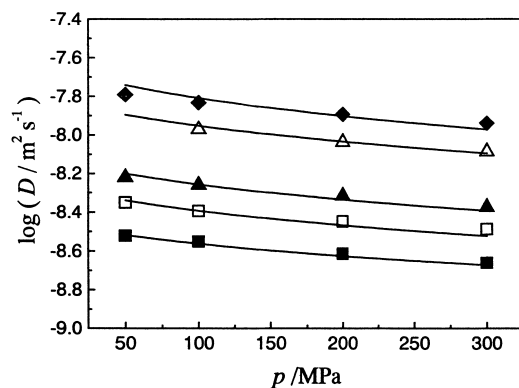


Fig. 10. The logarithms of the self-diffusion coefficient for liquid hydrogen fluoride as a function of temperature and pressure. Solid lines refer to the calculated values, symbols refer to the experimental data [41]: (■) 243.9 K; (□) 265.0 K; (▲) 283.7 K; (△) 337.0 K; (◆) 374.1 K.

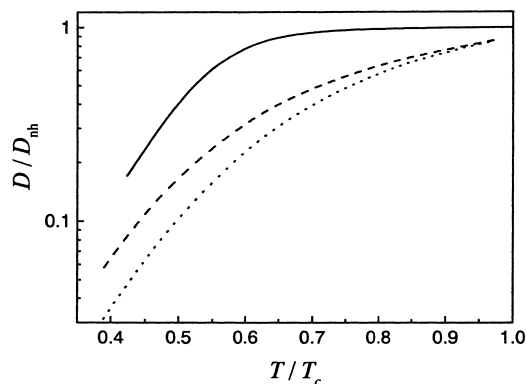


Fig. 11. The ratio of the experimental diffusion coefficient to the value of D_{nh} as a function of reduced temperature $T_r = T/T_c$, where D_{nh} is the self-diffusion coefficient in the case of no hydrogen bond. Solid line refers to that of water, dashed line refers to that of methanol, dotted line refers to that of ethanol.

The necessity to take into account the importance of the hydrogen bond is shown by the fact that if we try to fit the experimental data with the rough LJ model [2] or the LJC model [4], we obtain the values of AAD which are always greater than 30%. In the present self-diffusion coefficient equation, the role of the hydrogen bond is clearly shown. We are able to connect the X^A values derived from the SAFT with the self-diffusion behavior. To show quantitatively the importance of the hydrogen bond on the diffusion coefficient along the saturation line, the behavior of the ratio of the experimental diffusion coefficient to the value of D_{nh} is plotted in Fig. 11 against reduced temperature for water, methanol and ethanol. According to Fig. 11, water at $T^* > 0.78$ appears to be devoid of hydrogen-bonds. This is validated by the infra-red spectra data of Luck [45]. When the temperature approaches to the critical temperature, the percentage of non-hydrogen-bonded H_2O molecules determined by 0.9488- and 1.140 μ -infra-red bands is near 100%.

4. Conclusion

In this work, an equation for the self-diffusion coefficient of an associating LJC 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 Lennard–Jones 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 Lennard–Jones 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 total average absolute deviation is 6.69% for 10 associating substances studied in this work. These show that the proposed equation can be used to calculate the self-diffusion coefficient for associating substances with good accuracy.

List of symbols

AAD average absolute deviation defined by Eq. (22)

A, B, C association site A, B, C

C	proportional constant
c	$N_A C$ (J/mol)
D	self-diffusion coefficient (m^2/s)
d	effective hard sphere diameter (nm)
E_b	relative barrier height (J)
$F(N, \rho^*)$	correction function for HSC fluid
$f(\rho^*)$	correction function for HS fluid
$g(d)$	radial distribution function at contact
k	Boltzmann constant (1.381×10^{-23} J/K)
M	molecular mass (g/mol)
m	mass of a segment (g)
N	chain length
N_A	Avogadro number (6.022×10^{23} molecules/mol)
NDP	number of data points
OF	objective function
p	pressure (MPa)
R	universal gas constant (8.3144 J/(mol K))
T	temperature (K)
T^*	reduced temperature
X^A	mole fraction of molecules not bonded at site A

Greek letters

Δ	strength of interaction between two association sites (nm^3)
ε	Lennard–Jones segment energy (J)
ε^{HB}	association energy of hydrogen bonding (J)
γ	$(N - 1)/N$
η	$\pi \rho N d^3 / 6$ for real fluids
κ^{HB}	volume of interaction between two association sites
ρ	number density of a molecule (nm^3)
σ	Lennard–Jones segment diameter (nm)

Subscripts

b	barrier
C	chain
c	critical state
LJC	Lennard–Jones chain
nh	non-associating fluid
r	reduced quantity
0C	chain fluid at very low gas density

Superscripts

A, B	association site A, B
cal	calculated value
exp	experimental value

HB	hydrogen bond
OH	O–H bond
*	reduced quantity

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References

- [1] J.H. Dymond, *Chem. Soc. Rev.* 14 (1985) 317–356.
- [2] E. Ruckenstein, H. Liu, *Ind. Eng. Chem. Res.* 36 (1997) 3927–3936.
- [3] D. Chandler, *J. Chem. Phys.* 62 (1975) 1358–1363.
- [4] Y.-X. Yu, G.-H. Gao, *Fluid Phase Equilib.* 166 (1999) 111–124.
- [5] Y.-X. Yu, G.-H. Gao, *Int. J. Thermophys.* 21 (2000) 57–70.
- [6] N. Shaker-Gaafar, N. Karger, S. Wappmann, H.-D. Lüdemann, *Ber. Bunsenges. Phys. Chem.* 97 (1993) 805–811.
- [7] T.J. Speedy, F.X. Prielmeier, T. Vardag, E.W. Lang, H.-D. Lüdemann, *Mol. Phys.* 66 (1989) 577–590.
- [8] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 1709–1721.
- [9] Y. Marcus, *Fluid Phase Equilib.* 164 (1999) 131–142.
- [10] F.P. Ricci, M.A. Ricci, D. Rocca, *J. Chem. Phys.* 66 (1977) 5509–5512.
- [11] R. Lamanna, M. Delmelle, S. Cannistraro, *Phys. Rev. E* 49 (1994) 2841–2850.
- [12] S.H. Huang, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 2284–2294.
- [13] S.H. Huang, M. Radosz, *Ind. Eng. Chem. Res.* 30 (1991) 1994–2005.
- [14] W.G. Chapman, G. Jackson, K.E. Gubbins, *Mol. Phys.* 65 (1988) 1057–1079.
- [15] M.S. Wertheim, *J. Chem. Phys.* 87 (1987) 7323–7331.
- [16] Y.-X. Yu, J.-F. Lu, J.-S. Tong, Y.-G. Li, *Fluid Phase Equilib.* 102 (1994) 159–172.
- [17] H. Adidharma, M. Radosz, *Fluid Phase Equilib.* 161 (1999) 1–20.
- [18] P.K. Jog, A. Garcia-Cuellar, W.G. Chapman, *Fluid Phase Equilib.* 158 (1999) 321–326.
- [19] S.V. Lishchak, N.P. Malomuzh, *Chem. Phys. Lett.* 309 (1999) 307–313.
- [20] P. Hanggi, *J. Stat. Phys.* 42 (1986) 105–148.
- [21] N.F. Carnahan, K.E. Starling, *J. Chem. Phys.* 51 (1969) 635–636.
- [22] D. Ben-Amotz, D.R. Herschbach, *J. Phys. Chem.* 94 (1990) 1038–1047.
- [23] M.A. Gonzalez, B. Enciso, F.J. Bermejo, M. Bee, *J. Chem. Phys.* 110 (1999) 8045–8059.
- [24] K.R. Harris, L.A. Woolf, *J. Chem. Soc., Faraday Trans. I* 76 (1980) 377–385.
- [25] W.J. Lamb, G.A. Hoffman, J. Jonas, *J. Chem. Phys.* 74 (1981) 6875–6880.
- [26] F.A.L. Dullien, *AIChE J.* 18 (1972) 62–70.
- [27] R. Mills, *J. Phys. Chem.* 77 (1973) 685–688.
- [28] K. Krynicki, C.D. Green, D.W. Sawyer, *Faraday Discuss. Chem. Soc.* 66 (1979) 199–208.
- [29] T. Grindley, J.B. Lind Jr., *J. Chem. Phys.* 54 (1971) 3983–3989.
- [30] N.B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, Hemisphere, Washington, DC, 1975.
- [31] D.J. Wilbur, T. DeFries, J. Jonas, *J. Chem. Phys.* 65 (1976) 1783–1786.
- [32] N. Karger, T. Vardag, H.-D. Lüdemann, *J. Chem. Phys.* 93 (1990) 3437–3444.
- [33] R.L. Hurle, A.J. Easteal, L.A. Woolf, *J. Chem. Soc., Faraday Trans. I* 81 (1985) 769–779.
- [34] I. Cibulka, M. Zikova, *J. Chem. Eng. Data* 39 (1994) 876–886.
- [35] I. Cibulka, *Fluid Phase Equilib.* 89 (1993) 1–18.
- [36] D. Ambrose, J. Walton, *Pure Appl. Chem.* 61 (1989) 1395–1403.

- [37] S. Meckl, M.D. Zeidler, *Mol. Phys.* 63 (1988) 85–95.
- [38] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, 1987.
- [39] N. Karger, T. Vardag, N. Shakergafar, H.-D. Lüdemann, *J. Mol. Liq.* 64 (1995) 211–219.
- [40] S. Wappmann, N. Karger, H.-D. Lüdemann, *J. Chem. Eng. Data* 40 (1995) 233–236.
- [41] N. Karger, T. Vardag, H.-D. Lüdemann, *J. Chem. Phys.* 100 (1994) 8271–8276.
- [42] N. Karger, H.-D. Lüdemann, *J. Chem. Phys.* 109 (1998) 3301–3303.
- [43] T.-H. Chung, L.L. Lee, K.E. Starling, *Ind. Eng. Chem. Fundam.* 23 (1984) 8–13.
- [44] T.E. Daubert, R.P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Hemisphere, New York, 1989.
- [45] W.A.P. Luck, *Discuss. Faraday Soc.* 43 (1967) 115–127.