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New Equations for Tracer Diffusion Coefficients of Solutes in Supercritical and Liquid Solvents Based on the Lennard-Jones Fluid Model

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In this paper, on the basis of our recent works on self-diffusion coefficients of Lennard-Jones and real fluids, prediction and correlation models are proposed for the representation of tracer diffusivities of solutes in liquids and supercritical fluids. It has been found that with the parameters obtained from self-diffusion data (the Lennard-Jones energy and diameter) it is possible to predict the tracer coefficients with acceptable accuracy by means of simple combining rules. Moreover, two correlation models involving only one binary parameter (for energy and diameter corrections, respectively) are proposed. Both models exhibit accuracies well inside the experimental uncertainties and give results comparable to the two-parameter Dymond-modified Hildbrand–Batschinski equation.

Introduction

The design of chemical reactors and separation processes involving interface mass transfer often requires the knowledge of binary diffusion coefficients. It is well-known that the lack of fundamental transport properties data has hindered the development of the supercritical fluid (SCF) extraction to a substantial commercial level. In addition, the mutual diffusivities are of great importance in providing information regarding the kind of interactions between unlike molecules.

The theories describing the diffusional mass transfer in dense gases and liquids are less developed than their counterparts in solids and dilute gases, owing to the irregularity of their molecular arrangement. Most of the existing models are based on hydrodynamic theory, kinetic theory, absolute-rate theory of Eyring, free volume theory, and models devised for simple idealized fluids.

With respect to the successful free volume theory, one may say, succinctly, that the devised equations are very simple, have a theoretical background, involve a small number of parameters (usually four at most), and have a broad range of applicability (dense gases, liquids, and supercritical phase). Following the original work of Batschinski (1913) for real liquids, later reestablished by Hildbrand (1971), the diffusion of a solute (2) at infinite dilution in solvent (1) will obey an equation of the form

$$D_{12} = B' V_f = B'(V_{11} - V_D) \quad (1)$$

where B' is a constant characteristic of the solute–solvent pair, V_D is a constant related primarily with the solvent, V_f is the free volume, and V_{11} is the solvent molar volume. The results obtained by Dymond (1974) for the self-diffusivity of hard spheres prompted Chen et al. (1982) to suggest that instead of eq 1 the preferred equation should be

$$D_{12} = B\sqrt{T}(V_{11} - V_D) \quad (2)$$

where T is the absolute temperature. This model, hereafter referred to as DHB (Dymond–Hildbrand–Batschinski), exhibits quite different V_D s for the same solvent, which means they are system specific and, sometimes, even negative values. Such physically meaningless results have been also found in the present work.

In this work we approach the problem of tracer diffusion in liquids, dense gases, and supercritical fluids, applying the formalism of the kinetic theory of gases (Chapman and Cowling, 1970): substitute all pure parameters in a self-property equation by binary parameters obtained from appropriate combining rules. Salim and Trebble (1995) have implemented this analysis in the study of infinite dilution diffusivities of n -alkanes with the interacting-sphere model for self-diffusion. In this paper we chose the two-parameter equation of Liu–Silva–Macedo (LSM) (Liu et al., 1996), because of its success in describing self-diffusivities of real fluids, except hydrogen-bonding molecules (absolute average deviation, AAD = 5.45%, for 2047 data points; its scope has been proven to comprehend molecules as polar as acetonitrile and nonspherical as n -hexadecane). In addition, two correlation models are proposed, both involving only one binary parameter, for energy and molecular diameter, respectively. The DHB equation has been adopted for comparison, owing to being one of the most popular equations for the representation of diffusion in liquids and SCFs. Other reference equations have not been chosen, as they are either specific to some solvents (for example, CO₂) or require predicted viscosities or are limited to a determined phase or density range.

Models Proposed in This Work

The Lennard-Jones (LJ) model of Liu–Silva–Macedo (LSM) (Liu et al., 1996) for self-diffusion coefficients, D_{11} , is

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$$D_{11} = 21.16 \left(\frac{1000RT}{M_{11}} \right)^{1/2} \frac{V_{11}}{N_a (\sigma_{11}^{\text{eff}})^2} \times \exp \left(-\frac{0.75\rho_{11}^*}{1.2588 - \rho_{11}^*} - \frac{0.27862}{T_{11}^*} \right) \quad (3)$$

where M_{11} is the molecular weight in g/mol, V_{11} is the molar volume in cm³/mol, N_a is Avogadro's constant, and ρ_{11}^* and T_{11}^* are the reduced density and temperature, respectively:

$$\rho_{11}^* = \rho (\sigma_{11}^{\text{LJ}})^3 = \frac{N_a}{V_{11}} (\sigma_{11}^{\text{LJ}})^3 \quad (4)$$

$$T_{11}^* = \frac{T}{\epsilon_{11}^{\text{LJ}}/k} \quad (5)$$

Finally, σ_{11}^{eff} in eqs 3 and 4 is the effective hard sphere diameter given by

$$\sigma_{11}^{\text{eff}} = 2^{1/6} \sigma_{11}^{\text{LJ}} [1 + (1.3229 T_{11}^*)^{1/2}]^{-1/6} \quad (6)$$

Therefore, this model contains only two parameters: the pure component LJ energy ($\epsilon_{11}^{\text{LJ}}/k$, in K) and diameter (σ_{11}^{LJ} , in cm). For those substances whose self-diffusivities have been correlated with eq 3, the molecular parameters are taken from Liu et al. (1996). For other substances, the following generalized equations have been adopted to estimate these values (Silva et al., 1996)

$$\epsilon_{11}^{\text{LJ}}/k = 0.774 T_c \quad (7)$$

$$\sigma_{11}^{\text{LJ}} = 10^{-8} \left[0.17791 + 11.779 \frac{T_c}{P_c} - 0.049029 \left(\frac{T_c}{P_c} \right)^2 \right]^{1/3} \quad (8)$$

where T_c and P_c are the critical temperature (in K) and pressure (in bar), respectively.

In view of the reliable representations accomplished by the LSM model, we propose an empirical extension of eq 3 to calculate the limiting mutual diffusion coefficients, D_{12}

$$D_{12} = 21.16 \left(\frac{1000RT}{M_{12}} \right)^{1/2} \frac{V_{11}}{N_a (\sigma_{12}^{\text{eff}})^2} \times \exp \left(-\frac{0.75\rho_{11}^*}{1.2588 - \rho_{11}^*} - \frac{0.27862}{T_{12}^*} \right) \quad (9)$$

T_{12}^* and σ_{12}^{eff} are still calculated by, respectively, eqs 5 and 6 but presently defined in terms of the binary LJ parameters σ_{12}^{LJ} and $\epsilon_{12}^{\text{LJ}}$. M_{12} is the reduced mass of the system

$$M_{12} = \frac{2M_{11}M_{22}}{M_{11} + M_{22}} \quad (10)$$

Prediction Model (TLSM). The energy combining rule proposed in this work is different from those presented in literature (Salim and Trebble, 1995), in order to reduce the interaction energy. For the diam-

eter, the classical empirical law has been adopted. Thus

$$\epsilon_{12}^{\text{LJ}}/k = \sqrt{(\sigma_{11}^{\text{LJ}})^3 (\epsilon_{11}^{\text{LJ}}/k) (\sigma_{22}^{\text{LJ}})^3 (\epsilon_{22}^{\text{LJ}}/k) / (\sigma_{12}^{\text{LJ}})^3} \quad (11)$$

$$\sigma_{12}^{\text{LJ}} = \frac{\sigma_{11}^{\text{LJ}} + \sigma_{22}^{\text{LJ}}}{2} \quad (12)$$

This model will henceforth be labeled TLSM (Tracer Liu–Silva–Macedo).

Correlation Model with Interaction Energy Parameter (TLSM_{en}). The combining rule for $\epsilon_{12}^{\text{LJ}}/k$ is

$$\epsilon_{12}^{\text{LJ}}/k = (1 - k_{12}^{\text{en}}) \sqrt{(\sigma_{11}^{\text{LJ}})^3 (\epsilon_{11}^{\text{LJ}}/k) (\sigma_{22}^{\text{LJ}})^3 (\epsilon_{22}^{\text{LJ}}/k) / (\sigma_{12}^{\text{LJ}})^3} \quad (13)$$

where k_{12}^{en} is an adjustable parameter and σ_{12}^{LJ} is given by eq 12.

Correlation Model with Interaction Diameter Parameter (TLSM_d). The combining rule for σ_{12}^{LJ} is

$$\sigma_{12}^{\text{LJ}} = (1 - k_{12}^{\text{d}}) \frac{\sigma_{11}^{\text{LJ}} + \sigma_{22}^{\text{LJ}}}{2} \quad (14)$$

where k_{12}^{d} is an adjustable parameter and $\epsilon_{12}^{\text{LJ}}/k$ is given by eq 11 with its appearing σ_{12}^{LJ} defined by eq 12, that is

$$\epsilon_{12}^{\text{LJ}}/k = \frac{8 \sqrt{(\sigma_{11}^{\text{LJ}})^3 (\epsilon_{11}^{\text{LJ}}/k) (\sigma_{22}^{\text{LJ}})^3 (\epsilon_{22}^{\text{LJ}}/k)}}{(\sigma_{11}^{\text{LJ}} + \sigma_{22}^{\text{LJ}})^3} \quad (15)$$

Sources of Data

The aim of this work was the development of equations for the representation of limiting mutual diffusion coefficients of solutes in supercritical and liquid solvents. With this purpose the largest database ever used has been compiled: 77 binary systems performing 1033 data points. Table 1 contains the systems studied, along with the data sources, number of data points (NDP), and reduced ranges of temperature, pressure, and density for each system.

As much as possible, all published data were used. However, systems with less than four experimental points reported have been rejected, as well as data available only in graphical form. In addition, when a comparison from different sources clearly showed that some values were erroneous, these points were excluded from the calculations. Such question concerns especially tracer diffusivities in SCFs, where truly large deviations, or even inconsistencies, may be found, notwithstanding the low uncertainties inside individual determinations—usually 5–8% error for chromatographic peak-broadening measurements. By way of illustration, diffusion coefficients of 3-pentanone published by the same research group have been plotted in Figure 1. In this particular case the values at $T = 314$ K were rejected, since they violate the general trend expected: binary diffusivities increase with increasing temperature.

Calculation Results

In Table 2 all data necessary for the calculations are listed. Table 3 shows a compilation of the detailed results obtained with the three models proposed in this paper (TLSM, eqs 9 + 11 + 12; TLSM_{en}, eqs 9 + 12 + 13; TLSM_d, eqs 9 + 14 + 15) and the equation adopted for comparison (DHB, eq 2).

Table 1. Systems Studied and Data Sources

system		T_r	P_r	ρ_r	NDP	data sources	
solvent	solute						
ethylene (C ₂ H ₄)	carbon dioxide	1.056–1.233	0.217–3.724	0.051–1.593	49	<i>a</i>	
carbon dioxide (CO) ₂	ethylene	0.980–1.145	0.148–3.159	0.037–1.747	48	<i>a</i>	
	<i>n</i> -pentane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -hexane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -heptane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -octane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -nonane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -decane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -undecane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -dodecane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	<i>n</i> -tetradecane	0.983–1.013	1.235–1.441	1.562–1.748	5	<i>b</i>	
	benzene	0.997–1.095	1.098–4.804	0.598–2.001	43	<i>c, d, e</i>	
	toluene	1.013–1.095	1.104–4.804	0.703–2.001	29	<i>d, f</i>	
	ethylbenzene	1.029–1.095	2.059–4.804	1.298–2.001	15	<i>d</i>	
	<i>n</i> -propylbenzene	1.029–1.095	2.059–4.804	1.298–2.001	34	<i>c, d</i>	
	<i>i</i> -propylbenzene	1.029–1.095	2.059–4.804	1.298–2.001	15	<i>d</i>	
	1,3,5-trimethylbenzene	0.997–1.095	1.167–3.638	0.762–1.889	17	<i>c, e</i>	
	naphthalene	0.915–1.095	0.922–13.727	1.082–2.378	44	<i>e, g, h</i>	
	phenanthrene	0.997–1.095	1.579–3.638	1.090–1.881	7	<i>e</i>	
	phenol	1.013–1.078	1.104–1.985	0.703–1.719	21	<i>f</i>	
	diethyl ether	1.029–1.095	1.098–2.196	0.417–1.707	15	<i>i</i>	
	diisopropyl ether	1.029–1.095	1.098–2.196	0.419–1.707	15	<i>i</i>	
	tetrahydrofuran	1.029–1.095	1.098–2.196	0.419–1.707	15	<i>i</i>	
	acetone	0.983–1.095	1.235–3.638	1.084–1.889	21	<i>b, e, k</i>	
	2-butanone	1.033	1.304–2.471	1.173–1.741	15	<i>k</i>	
	2-pentanone	1.033	1.304–2.471	1.173–1.741	14	<i>k</i>	
	3-pentanone	1.029–1.033	1.373–2.334	1.299–1.701	20	<i>k</i>	
	benzoic acid	0.982–1.048	0.975–3.445	1.148–1.836	7	<i>l</i>	
	ethyl acetate	1.013–1.078	1.038–1.963	0.455–1.723	15	<i>f</i>	
	DHA methyl ester	1.013–1.045	1.327–2.889	1.290–1.819	17	<i>m</i>	
	DHA ethyl ester	1.013–1.045	1.327–2.889	1.290–1.819	17	<i>m</i>	
	EPA methyl ester	1.013–1.045	1.327–2.889	1.290–1.819	17	<i>m</i>	
	caffeine	1.013–1.078	1.102–1.968	0.913–1.723	21	<i>f</i>	
	chlorotrifluoromethane (CClF ₃)	<i>p</i> -xylene	1.053	1.222–2.819	0.691–1.727	8	<i>j</i>
		acetone	1.037	1.150–2.093	0.687–1.651	10	<i>j</i>
	sulfur hexafluoride (SF ₆)	carbon tetrachloride	1.029	1.117–3.816	0.681–1.906	6	<i>j</i>
		benzene	1.029	0.931–3.816	0.408–1.906	9	<i>j</i>
	toluene	1.029	0.931–3.816	0.408–1.906	11	<i>j</i>	
	<i>p</i> -xylene	0.888–1.061	0.798–3.989	0.408–2.246	52	<i>j</i>	
	1,3,5-trimethylbenzene	1.029	1.117–3.816	0.681–1.906	10	<i>j</i>	
	naphthalene	0.998–1.030	1.729–3.191	1.509–2.028	5	<i>n</i>	
	benzoic acid	1.030–1.061	1.729–3.191	1.248–1.906	6	<i>n</i>	
	benzene	1.046–1.096	1.710–5.080	1.432–1.908	11	<i>o</i>	
2,3-dimethylbutane (2,3-DMB)	toluene	1.046–1.096	2.005–5.080	1.432–1.908	10	<i>o</i>	
	naphthalene	1.046–1.096	1.710–5.080	1.432–1.908	9	<i>o</i>	
	phenanthrene	1.046–1.096	1.710–5.080	1.432–1.908	11	<i>o</i>	
	benzene	0.539–0.945	3.93; sat.p. ^{<i>u</i>}	1.757–2.862	12	<i>p, q</i>	
cyclohexane (cC ₆)	toluene	0.539–0.945	3.93; sat.p.	1.757–2.862	12	<i>p, q</i>	
	<i>p</i> -xylene	0.539–0.945	sat.p.	1.757–2.833	8	<i>p</i>	
	1,3,5-trimethylbenzene	0.539–0.945	3.93; sat.p	1.757–2.862	12	<i>p, q</i>	
	naphthalene	0.539–0.945	3.93; sat.p	1.757–2.862	12	<i>p, q</i>	
	phenanthrene	0.539–0.945	sat.p.	1.757–2.833	8	<i>p</i>	
	carbon disulfide	0.588	0.332–127.58	2.812–3.467	10	<i>r</i>	
<i>n</i> -hexane (<i>n</i> C ₆)	benzene	0.588–1.070	<i>v</i>	1.348–3.459	31	<i>q, r, s</i>	
	toluene	0.588–1.070	<i>w</i>	1.348–3.459	28	<i>q, r, s</i>	
	<i>m</i> -xylene	0.597–0.657	0.498; 0.532	2.752–2.864	5	<i>q</i>	
	<i>p</i> -xylene	0.617–1.070	<i>x</i>	1.348–2.864	17	<i>q, s</i>	
	1,3,5-trimethylbenzene	0.597–1.070	<i>x</i>	2.752–2.864	20	<i>q, s</i>	
	naphthalene	0.597–1.070	<i>x</i>	1.348–2.864	20	<i>q, s</i>	
	phenanthrene	0.657–1.070	sat.p.; $P_r > 1$	1.348–2.671	15	<i>s</i>	
	acetone	0.597–0.657	0.498; 0.532	2.752–2.864	5	<i>q</i>	
	acetonitrile	0.588	0.034–128.11	2.812–3.467	7	<i>r</i>	
	<i>n</i> -octane	0.553–0.883	0.037–1.268	2.235–2.929	4	<i>t</i>	
<i>n</i> -heptane (<i>n</i> C ₇)	<i>n</i> -decane	0.553–0.883	0.037–1.268	2.235–2.929	5	<i>t</i>	
	<i>n</i> -dodecane	0.553–0.883	0.037–1.296	2.235–2.944	5	<i>t</i>	
	<i>n</i> -tetradecane	0.553–0.883	0.037–1.296	2.235–2.944	5	<i>t</i>	
	<i>n</i> -hexadecane	0.553–0.883	0.037–1.296	2.164–2.944	8	<i>t</i>	
<i>n</i> -dodecane (<i>n</i> C ₁₂)	benzene	0.461–0.506	8.790	3.068–3.152	4	<i>q</i>	
	toluene	0.461–0.506	8.790	3.068–3.152	4	<i>q</i>	
	<i>m</i> -xylene	0.461–0.506	8.790	3.068–3.152	4	<i>q</i>	
	1,3,5-trimethylbenzene	0.461–0.506	8.790	3.068–3.152	4	<i>q</i>	
	naphthalene	0.461–0.521	8.790	3.039–3.152	5	<i>q</i>	
	<i>n</i> -octane	0.462–0.860	0.776–1.890	2.190–3.106	9	<i>t</i>	

Table 1 (Continued)

system		T_r	P_r	ρ_r	NDP	data sources
solvent	solute					
	<i>n</i> -decane	0.462–0.860	0.776–0.796	2.190–3.106	5	<i>t</i>
	<i>n</i> -tetradecane	0.462–0.860	0.776–0.796	2.190–3.106	5	<i>t</i>
	<i>n</i> -hexadecane	0.462–0.860	0.776–0.796	2.190–3.106	5	<i>t</i>
	acetone	0.461–0.521	8.790	3.039–3.152	5	<i>q</i>

^a Takahashi and Hongo (1982). ^b Umezawa and Nagashima (1992). ^c Swaid and Schneider (1979). ^d Suárez et al. (1993). ^e Sassi et al. (1987). ^f Lai and Tan (1995). ^g Lamb et al. (1989). ^h Lauer et al. (1983). ⁱ Silva and Macedo (1994). ^j Knoper et al. (1987). ^k Dahmen et al. (1990a). ^l Catchpole and King (1994). ^m Liong et al. (1992). ⁿ Debenedetti and Reid (1986). ^o Sun and Chen (1985a). ^p Sun and Chen (1985b). ^q Funazukuri et al. (1994). ^r Dymond and Woolf (1982). ^s Sun and Chen (1985c). ^t Matthews and Akgerman (1987). ^u sat.p.: saturation pressure. ^v P_r from 0.034 to 122.69 and at saturation pressure. ^w P_r from 0.034 to 124.58 and at saturation pressure. ^x P_r = 0.498 and 0.532, at saturation pressure and other points at $P_r > 1$.

Table 2. Data for Pure Substances

substance	M_{11}	T_c (K)	P_c (bar)	σ_{11}^{LJ} (Å)	ϵ_{11}^{LJ}/k (K)
carbon dioxide	44.01	304.19	73.00	3.261 92	500.71
ethylene	28.05	282.40	50.40	4.048 38	169.08
<i>n</i> -pentane ^a	72.15	469.70	33.70	5.369 67	363.55
<i>n</i> -hexane	86.18	507.50	30.10	5.618 41	434.76
<i>n</i> -heptane	100.20	540.30	27.40	5.943 56	404.05
<i>n</i> -octane	114.23	568.80	24.90	6.173 28	478.32
<i>n</i> -nonane	128.26	594.60	22.90	6.430 57	497.35
<i>n</i> -decane	142.29	617.70	21.20	6.713 95	434.86
<i>n</i> -undecane ^a	156.30	637.00	19.90	6.889 33	493.04
<i>n</i> -dodecane	170.34	658.20	18.20	7.004 51	672.90
<i>n</i> -tetradecane ^a	198.39	693.00	14.40	7.682 86	536.38
<i>n</i> -hexadecane	224.43	717.00	13.30	7.364 80	1669.19
cyclohexane	84.16	553.50	40.70	5.730 75	224.87
2,3-dimethylbutane ^a	86.18	500.00	31.30	5.602 27	387.00
benzene	78.11	562.20	48.90	5.191 65	308.43
toluene	92.14	591.80	41.00	5.454 50	350.74
ethylbenzene ^a	106.17	617.20	36.00	5.725 72	477.71
<i>p</i> -xylene ^a	106.17	616.20	35.10	5.767 54	476.94
<i>m</i> -xylene ^a	106.17	617.10	35.40	5.755 07	477.64
<i>n</i> -propylbenzene ^a	120.19	638.20	32.00	5.996 24	493.97
<i>i</i> -propylbenzene ^a	120.19	631.20	32.10	5.970 57	488.55
1,3,5-trimethylbenzene ^a	120.19	664.50	34.50	5.933 17	514.32
naphthalene ^a	128.17	748.40	40.50	5.858 74	579.26
phenanthrene ^a	178.20	873.00	32.40 ^c	6.557 37	675.70
caffeine ^a	194.20	803.40 ^b	33.30 ^b	6.348 12	621.83
phenol ^a	94.11	694.20	61.30	5.030 26	537.31
diethyl ether ^a	74.12	466.70	36.40	5.231 05	361.22
diisopropyl ether ^a	102.18	500.30	28.80	5.748 91	387.23
tetrahydrofuran ^a	72.11	540.10	51.90	4.897 19	418.04
acetone	58.08	508.10	47.00	4.670 12	332.97
2-butanone ^a	72.11	536.80	42.10	5.221 95	415.48
2-pentanone ^a	86.13	561.10	36.90	5.517 33	434.29
3-pentanone ^a	86.13	561.00	37.30	5.498 58	434.21
benzoic acid ^a	122.10	752.00	45.60	5.657 63	582.05
ethyl acetate ^a	88.11	523.20	38.30	5.336 06	404.96
DHA methyl ester ^a	342.50	852.40 ^c	10.35 ^c	8.607 47	659.76
DHA ethyl ester ^a	356.50	867.10 ^c	11.02 ^c	8.542 81	671.14
EPA methyl ester ^a	316.50	823.40 ^c	11.34 ^c	8.420 06	637.31
carbon tetrachloride	153.82	556.40	45.60	5.292 40	418.84
sulfur hexafluoride	146.05	318.70	37.60	4.766 29	271.68
carbon disulfide	76.13	552.00	79.00	4.299 01	376.51
chlorotrifluoromethane	104.46	302.00	38.70	4.376 36	410.79
acetonitrile	41.05	545.50	48.30	4.024 24	652.53

^a Lennard-Jones parameters (diameter and energy) estimated according to Silva et al. (1996). ^b Estimated by the Joback method (Reid et al., 1987). ^c From Liu and Macedo (1995).

In Table 4 the average results for the supercritical and liquid systems are given (supercritical, C₂H₄, CO₂, CClF₃, SF₆, 2,3-DMB; liquid, cC₆, nC₆, nC₇, nC₁₂).

A few authors do not report the densities for carbon dioxide. In these cases they have been calculated using the empirical correlation of Pitzer and Schreiber (1988), since it exhibits excellent agreement very near the critical point.

Discussion

The three models suggested in this paper extend our previous work (Liu et al., 1996) centered on LJ self-

diffusion coefficients to the infinitely diluted binary case, following the combining rules formalism of the kinetic theory of gases (Chapman and Cowling, 1970), in much the same way as Salim and Trebble (1995) did. The legitimacy of this extension emerges from the reliable results furnished by the self-diffusion equation employed.

With regard to the first proposed model (TLISM), we detach the following comments: (1) It is a merely predictive model. The only input data required are the temperature, the solvent density, and, for both components, the molecular weight and the LJ force constants.

Table 3. Calculation Results

system		NDP	TLSM	TLSM _{en}		TLSM _d		DHB		
solvent	solute		AAD	K_{12}^{en}	AAD	K_{12}^d	AAD	$B \times 10^7$	V_D	AAD
C ₂ H ₄ CO ₂	carbon dioxide	49	7.32	0.028 94	7.28	-0.004 88	7.27	3.0974	5.29	3.52
	ethylene	48	9.60	-0.278 22	5.12	-0.047 51	5.18	2.9026	-3.87	4.79
	<i>n</i> -pentane	5	20.78	0.428 02	3.29	0.096 61	3.15	4.0589	35.83	1.67
	<i>n</i> -hexane	5	29.46	0.607 74	3.00	0.148 99	2.85	3.9841	35.55	2.09
	<i>n</i> -heptane	5	33.06	0.723 30	3.55	0.175 61	3.31	3.9423	35.67	1.00
	<i>n</i> -octane	5	38.38	0.779 81	3.83	0.202 86	3.65	4.1530	37.05	1.66
	<i>n</i> -nonane	5	41.27	0.834 07	3.93	0.222 51	3.65	4.0607	37.02	1.43
	<i>n</i> -decane	5	41.44	0.861 56	3.96	0.225 32	3.70	3.8445	36.48	1.48
	<i>n</i> -undecane	5	44.35	0.884 43	4.76	0.242 25	4.48	4.1555	38.28	1.85
	<i>n</i> -dodecane	5	47.20	0.884 31	5.73	0.259 36	5.40	4.3508	39.93	3.00
	<i>n</i> -tetradecane	5	43.50	0.896 47	8.06	0.246 96	7.77	4.3701	41.99	3.32
	benzene	43	9.19	0.039 87	9.03	0.007 80	9.03	1.1224	-13.70	9.94
	toluene	29	11.31	0.241 60	5.07	0.049 46	5.10	1.3285	0.48	6.32
	ethylbenzene	15	17.50	0.394 05	2.08	0.091 52	2.07	1.8248	18.85	2.28
	<i>n</i> -propylbenzene	34	15.07	0.317 34	9.52	0.073 71	9.46	0.8647	-17.49	5.03
	<i>i</i> -propylbenzene	15	17.97	0.404 38	2.12	0.093 59	2.23	1.6274	17.00	2.00
	1,3,5-trimethylbenzene	17	14.98	0.191 35	13.70	0.045 70	13.66	0.7266	-30.12	7.82
	naphthalene	44	20.68	0.475 83	7.64	0.122 10	7.93	1.6782	18.13	7.28
	phenanthrene	7	27.91	0.549 96	3.97	0.142 90	3.80	1.5452	18.89	4.98
	phenol	21	11.39	0.175 50	7.79	0.045 23	7.80	1.0232	-19.06	5.52
	diethyl ether	15	16.97	-0.100 92	16.58	-0.020 81	16.55	1.0475	-26.57	4.98
	diisopropyl ether	15	14.80	0.163 69	12.56	0.034 01	12.61	1.0781	-16.30	7.87
	tetrahydrofuran	15	14.87	0.068 23	14.67	0.015 50	14.70	1.1871	-22.19	4.99
	acetone	21	12.99	0.166 02	10.38	0.037 01	10.36	2.7511	21.17	11.97
	2-butanone	15	38.02	0.820 13	5.04	0.212 43	5.04	3.6337	27.82	3.16
	2-pentanone	14	40.14	0.841 54	5.00	0.221 62	5.00	3.5454	29.16	2.65
	3-pentanone	20	40.95	0.851 06	4.51	0.226 48	4.51	3.8953	31.22	2.72
	benzoic acid	7	25.05	0.523 37	3.10	0.133 48	3.28	1.5072	9.17	2.39
	ethyl acetate	15	19.65	0.079 62	19.60	0.017 30	19.64	0.8254	-49.61	6.71
	DHA methyl ester	17	22.59	0.522 55	3.11	0.119 70	3.00	1.2079	25.70	0.92
	DHA ethyl ester	17	21.23	0.470 66	3.09	0.107 92	2.99	1.2010	26.01	0.87
	EPA methyl ester	17	21.00	0.481 93	3.67	0.110 65	3.63	1.2964	27.43	0.49
	caffeine	21	11.51	0.207 22	8.05	0.050 15	8.05	0.7164	-17.53	4.87
CClF ₃	<i>p</i> -xylene	8	23.14	-0.522 27	11.82	-0.121 74	11.82	0.4851	-13.32	2.28
	acetone	10	26.73	-0.697 08	5.96	-0.145 36	5.96	0.9096	19.58	2.56
SF ₆	carbon tetrachloride	6	3.24	-0.028 46	3.18	-0.005 31	3.18	0.6877	35.40	5.18
	benzene	9	14.27	-0.211 13	8.42	-0.035 09	8.42	0.6679	1.44	10.58
	toluene	11	14.35	-0.367 51	11.40	-0.063 45	11.40	0.5288	-18.56	9.73
	<i>p</i> -xylene	52	9.78	0.151 73	7.46	-0.033 04	7.58	0.5781	19.72	12.40
	1,3,5-trimethylbenzene	10	11.26	-0.212 56	10.37	-0.042 18	10.37	0.5377	18.96	4.59
	naphthalene	5	15.98	0.366 74	5.60	0.079 80	5.47	1.1687	67.42	5.52
2,3-DMB	benzoic acid	6	12.30	-0.322 41	5.03	-0.065 93	4.99	0.6061	40.87	2.61
	benzene	11	8.74	-0.288 48	1.64	-0.038 17	1.65	0.9661	70.08	1.56
	toluene	10	5.32	-0.203 63	1.40	-0.028 92	1.41	0.9458	77.91	1.79
	naphthalene	9	3.05	0.080 00	2.08	0.013 41	2.07	0.7527	66.74	1.75
	phenanthrene	11	5.49	0.163 23	2.90	0.029 30	2.91	0.5871	54.23	1.53
cC ₆	benzene	12	6.35	0.135 55	5.83	0.011 16	6.12	1.4520	101.34	3.04
	toluene	12	8.98	0.276 86	7.11	0.041 52	7.95	1.3305	100.99	2.84
	<i>p</i> -xylene	8	10.86	0.289 98	6.96	0.028 81	7.65	1.2210	100.22	3.88
	1,3,5-trimethylbenzene	12	8.09	0.212 76	6.10	0.039 08	6.95	1.1194	101.54	2.42
	naphthalene	12	13.98	0.399 51	6.11	0.072 28	7.71	1.1611	101.24	2.99
	phenanthrene	8	13.58	0.373 75	5.06	0.048 05	6.35	0.9775	101.00	4.31
<i>n</i> C ₆	carbon disulfide	10	10.58	0.195 88	4.81	0.044 36	4.81	1.1409	102.23	4.66
	benzene	31	8.78	-0.160 42	6.12	-0.027 72	5.93	1.1322	103.77	15.05
	toluene	28	5.95	-0.075 62	5.49	-0.012 13	5.45	1.0354	102.80	16.17
	<i>m</i> -xylene	5	2.90	0.011 20	2.81	0.002 80	2.80	1.3600	115.15	2.00
	<i>p</i> -xylene	17	7.72	0.130 59	7.27	0.023 18	7.24	0.9088	93.68	16.35
	1,3,5-trimethylbenzene	20	5.22	-0.008 17	5.20	-0.001 40	5.21	0.8743	101.17	14.54
	naphthalene	20	9.51	0.208 46	6.23	0.040 50	6.67	0.8828	98.34	15.14
	phenanthrene	15	11.53	0.297 87	6.20	0.062 72	6.55	0.6767	81.65	11.81
	acetone	5	15.23	-0.300 30	2.32	-0.062 49	2.31	1.4801	111.01	3.03
	acetonitrile	7	5.85	0.000 28	5.85	0.000 08	5.85	1.1551	102.14	5.93
<i>n</i> C ₇	<i>n</i> -octane	4	4.34	0.064 17	2.38	0.015 72	2.11	1.1427	133.32	1.92
	<i>n</i> -decane	5	1.94	0.037 41	1.50	0.006 78	1.51	0.9631	132.45	1.65
	<i>n</i> -dodecane	5	8.84	0.158 84	2.17	0.036 46	2.04	0.8855	132.67	2.18
	<i>n</i> -tetradecane	5	4.95	0.087 02	1.76	0.021 36	1.82	0.8028	133.05	2.96
	<i>n</i> -hexadecane	8	21.96	0.340 35	2.00	0.110 41	2.80	0.7500	133.82	3.09
<i>n</i> C ₁₂	benzene	4	26.62	-0.520 83	1.01	-0.125 64	0.81	0.6766	214.82	1.30
	toluene	4	18.55	-0.369 08	1.51	-0.094 22	1.50	0.6372	214.93	2.02
	<i>m</i> -xylene	4	10.01	-0.173 75	1.42	-0.050 65	1.16	0.5477	214.25	1.54
	1,3,5-trimethylbenzene	4	17.43	-0.256 13	2.01	-0.088 83	1.57	0.4609	213.97	0.79
	naphthalene	5	3.86	-0.054 52	1.82	-0.016 20	1.77	0.5064	214.04	1.41
	<i>n</i> -octane	9	5.93	-0.133 71	2.26	-0.029 53	1.50	0.6640	218.97	1.48
	<i>n</i> -decane	5	6.85	-0.179 83	3.06	-0.031 73	2.20	0.5822	219.24	2.98
	<i>n</i> -tetradecane	5	6.50	-0.197 14	3.69	-0.040 36	3.70	0.4729	221.14	7.84
	<i>n</i> -hexadecane	5	16.96	0.249 46	2.52	0.085 06	4.46	0.4466	221.99	6.69
	acetone	5	32.07	-0.625 13	1.44	-0.148 59	1.17	0.8244	215.52	1.68

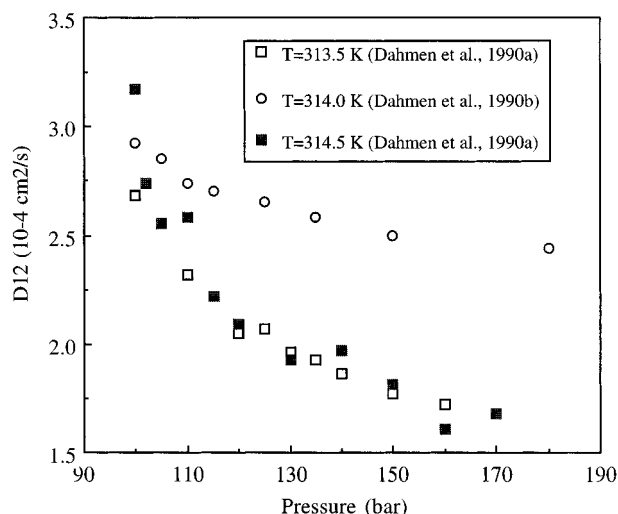


Figure 1. Example of inconsistencies found between available tracer diffusivities in SCF; illustration for 3-pentanone. (Note that the diffusion coefficients should increase with rising temperature.)

Table 4. Percent Deviations for Each Phase

solvent	NDP	prediction model	one-parameter models		two-parameter model
		TLSTM (present work) ^a	TLSTM _{en} (present work) ^b	TLSTM _d (present work) ^c	DHB (eq 2)
SCF	734	16.88	7.16	7.17	5.36
liquid	299	9.58	4.88	5.10	8.32
total	1033	14.77	6.50	6.57	6.22

^a Eqs 9 + 11 + 12. ^b Correlation model with energy parameter (eqs 9 + 12 + 13). ^c Correlation model with diameter parameter (eqs 9 + 14 + 15).

These last values are available for a large number of substances (Liu et al., 1996) or may be easily estimated from the knowledge of the critical temperature and pressure (Silva et al., 1996). (2) The calculation results in Table 4 show that the TLSTM equation is reliable for liquids and SCFs (grand AAD = 14.77%; maximum error = 47.20%). The better performance for liquids (AAD = 9.58%; maximum error = 32.07%) was expected in advance, since most self-diffusivity data used in the optimization of the LJ parameters refer to that state (Liu et al., 1996; Silva et al., 1996). (3) Taking into account the discrepancies or even incongruences observed between different published data for the same substance, we may consider the AAD found for supercritical solvents (AAD = 16.88%) an acceptable result. (4) This work does not include hydrogen-bonding solvents, since the LSM equation is not applicable in these cases. According to Silva et al. (1996), accurate self-diffusion predictions exact at least four parameters. (5) It is remarkable the good execution achieved for systems completely unknown, that is, with all LJ parameters estimated: AAD(2,3-DMB/naphthalene) = 3.05%, AAD(2,3-DMB/phenanthrene) = 5.49%. It is also surprising the satisfactory result attained for the very important system CO₂/caffeine (AAD = 11.51%), in light of the fact that the critical temperature and pressure and the LJ energy and molecular diameter have been estimated.

Concerning the one-parameter correlations presented in this paper, we emphasize the following points: (1) It has been found that both equations give similar results, (from Table 4, AAD_{en} = 6.50% and AAD_d = 6.57%), the type of correction performed (energy or diameter) being irrelevant. (2) The better performance for liquids closely resembles the pure predictive model mentioned above.

(3) One binary parameter seems sufficient for good representations of tracer diffusivities for all the systems studied, which makes them confident correlations. Its introduction has diminished significantly the AADs of the TLSTM prediction (please see the systems CO₂/*n*-alkanes), which reveals that these *k_{ij}*s go through the real interpretation of the diffusive phenomenon, akin to the thermodynamic binary corrections. (It is well-known that mixtures of hard spheres, whose components interact by a hard-core potential diameter given by eq 12, are possibly deprived of typical phenomena of fluid mixtures, such as demixing or partial mixing of the components). (4) Despite of possessing two parameters, the DHB equation (AAD = 6.22%) exhibits results comparable to our one-parameter correlations (AADs = 6.50% and 6.57%). Besides, this reference equation has presented two physically meaningless results: quite different minimum diffusive free volumes (*V_D*) for the same solvent and, sometimes, even negative values (please see Table 3).

Conclusions

In this paper we seek to interpret the diffusive phenomenon in terms of a LJ model. The related force constants (energy and diameter) should be obtained from our previous works (Liu et al., 1996; Silva et al., 1996).

According to the present results we recommend our prediction model (TLSTM) to estimate tracer diffusivities with acceptable accuracy, if there is no experimental data available. On the other hand, when a few data points can be found, one of our correlation models (TLSTM_{en} and TLSTM_d) can be used with confidence, by first optimizing one binary parameter. For liquids these models perform better than for SCFs, as discussed above.

Concerning DHB model, it has been realized that its interest is confined to correlative purposes, due to the physically meaningless regressed values of *V_D*. Nevertheless, in literature there have been many attempts to get predictive models by generalizing their two parameters (for instance, in terms of molecular weights and critical volume).

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Nomenclature

AAD = average absolute deviation:

$$(100/\text{NDP}) \sum_{i=1}^{\text{NDP}} |D_{12,i}^{\text{cal}} - D_{12,i}^{\text{exp}}| / D_{12,i}^{\text{exp}}$$

B = parameter in eqs 1 and 2

D = diffusion coefficient, cm²/s

DHB = Dymond–Hildbrand–Batschinski

k₁₂ = binary parameter

LJ = Lennard–Jones

TLSTM = Tracer Liu–Silva–Macedo equations suggested in this work

M = molecular weight, g/mol

N_a = Avogadro's constant

NDP = number of data points

P = pressure, bar

R = 8.3144 J/(mol K), gas constant

SCF = supercritical fluid

T = temperature, K
 V = molar volume, cm³/mol
 V_D = parameter in eqs 1 and 2
 V_f = free volume

Greek Letters

ϵ/k = Lennard-Jones energy parameter, K
 σ = Lennard-Jones molecular diameter, cm
 ρ = number density, cm⁻³

Subscripts

1 = solvent
 2 = solute
 11, 22 = pure property
 12 = binary property
 c = critical property
 d = refers to diameter correlation
 en = refers to energy correlation
 r = reduced property

Superscripts

* = reduced property
 eff = refers to the effective hard sphere diameter
 LJ = Lennard-Jones

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