Prediction of Binary Diffusion Coefficients of Solutes in Supercritical Solvents

Chao-Hong He
Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027, P. R. China

New correlations, based on the rough hard-sphere theory and an extensive literature database, were developed for the determination of the binary diffusion coefficients of liquid and solid solutes in supercritical solvents. The correlations were tested to predict 107 solute-solvent systems with good results. The input data required for the correlations are the solute molecular weight, temperature, density and the solvent basic properties (molecular weight, critical volume, and critical pressure).

Introduction

Mass transfer occurring in supercritical fluid processes depends on the molecular diffusion of solutes in supercritical solvents. Therefore, the ability to predict the binary diffusion coefficients in supercritical fluids is of considerable importance in the design and efficient operation of supercritical fluid processes.

Though correlations for this purpose are available in many forms (Eaton and Akgerman, 1997; Liu et al., 1997; Akgerman et al., 1996; Catchpole and King, 1994; Funazukuri et al., 1991), most of them are either specific to the given supercritical solvent, covered a limited density range, or give poor prediction results. The objective of this article, therefore, is to propose new equations to predict the binary diffusion coefficients in various supercritical solvents with better results.

Predictive Correlations

Infinite-dilution molecular diffusion coefficients in liquids are readily correlated by the molecular dynamics approach employing the rough hard-sphere theory of diffusion (Dymond, 1985; Easteal and Woolf, 1984). Since the theory is independent of the fluid state, it is applicable in the supercritical region as well.

The rough hard-sphere approach to diffusion results in the equation (Eaton and Akgerman, 1997)

$$D_{21}=\frac{3}{8n_1\sigma_{21}^2}\sqrt{\frac{k_BT(m_1+m_2)}{2\pi m_1m_2}}\left[\frac{D_{21,SHS}}{D_{21,E}}\right]_{MD}\frac{A_{21}}{g(\sigma_{21})} \quad (1)$$

where A_{21} is the translational rotational coupling parameter, m is the mass of single molecule, $g(\sigma_{21})$ is the radial distribution function, MD is molecular dynamics, SHS is soft hard spheres, and k_B is the Boltzmann constant.

According to the molecular dynamics simulations (Easteal and Woolf,1990), Eaton and Akgerman (1997) showed that

$$\frac{V_1}{V_0}\left[\frac{D_{21,SHS}}{D_{21,E}}\right]_{MD}\frac{1}{g(\sigma_{21})}=a\left(\frac{V_1}{V_0}\right)^k-b \quad (2)$$

where V_0 is the close-packed hard-sphere volume.

Substituting Eq. 2 into Eq. 1 gives

$$D_{21}=\frac{3aA_{21}V_0^{1-k}}{8(n_1V_1)\sigma_{21}^2}\sqrt{\frac{k_BT(m_1+m_2)}{2\pi m_1m_2}}\,[V_1^k-bV_0^k/a] \quad (3)$$

where n_1V_1 and k_B are constants, and T is temperature (K).

Designate

$$A\times10^{-10}=\frac{3aA_{21}V_0^{1-k}}{8(n_1V_1)\sigma_{21}^2}\sqrt{\frac{N_Ak_B(m_1+m_2)}{2\pi m_1}} \quad (4)$$

where N_A is the Avogadro number.

$$B=bV_0^k/a \quad (5)$$

Equation 3 can be reduced to

$$D_{21}=A\times10^{-10}(V_1^k-B)\sqrt{T/M_2} \quad (6)$$

Equation 6 was applied to correlate the infinite-dilution diffusion coefficients of liquid and solid solutes in supercritical solvents, where the solvent molar volume V_1 is obtained by 1,000 M_1/ρ_1 (if ρ_1 is not available with the quoted data source, V_1 is then calculated by the BWR equation of state (Perry, 1984)). The correlation results showed that the parameter k approximated to 1 if the reduced solvent density ρ_r ($\rho_r = \rho_1/\rho_{c1} = V_{c1}/V_1$) is greater than 1.2, but became lesser while ρ_r is lesser, and could be represented by

$$k = 1, \qquad \rho_r \geq 1.2 \tag{7}$$

$$k = 1 + (\rho_r - 1.2)/\sqrt{M_1}, \qquad \rho_r < 1.2 \tag{8}$$

where ρ is density (kg/m^3), k is a parameter, and M is a molecular mass (kg/kmol).

Thus, in Eq. 6, there are two constants, A and B, to be fitted from the diffusion coefficient data. With this purpose, the large database has been used: 107 binary systems performing 1,167 data points. Table 1 contains the systems studied, along with the data sources.

From the fitted results, it was found that the parameters A and B were approximately dependent on the properties of the solvent only. Further analysis shows that $B \approx 23$ and A can be approximated as

$$A = 0.61614 + 3.0902 \exp\left(-0.87756\sqrt{M_1 V_{c_1}}/P_{c_1}\right) \tag{9}$$

Therefore, the final binary diffusion coefficients of solutes in supercritical solvents is

$$D_{21} = \left[0.61614 + 3.0902 \exp\left(-0.87756\sqrt{M_1 V_{c_1}}/P_{c_1}\right)\right] \times 10^{-10}(V_1^k - 23)\sqrt{T/M_2} \tag{10}$$

Prediction Results and Discussions

Equations 10, 7 and 8 have been used to predict the binary diffusion coefficients of all the solute-solvent systems given in Table 1. The total average absolute deviation (AAD%) is 7.5% for 1,167 data points with the density range $\rho_r \geq 0.21$, and the maximum AAD% is 24.9%, where the AAD% is

Table 1. Systems Studied* and Data Sources

Solvent: carbon dioxide	$Tr = 1.00$–1.13, $\rho_r = 0.43$–2.23, $N = 794$ 71 solutes: benzene (1–8), naphthalene (1,5,6,9–12), phenanthrene (1,9,13), toluene (4,5,14), ethylbenzene (4,5), (o-, m-, p-)xylene (5), *n*-propylbenzene (2,4,5), isopropylbenzene (4,5), mesitylene (1,2,5), pyrene (1), chrysene (1), ethylacetate (5,14), (C4:0, C8:0, C10:0, C14:0, C16:0, C18:0, C22:0, C22:6) ethyl ester (15) (C20:5, C22:6, C18:2, C14:1, C20:1, C22:1) methyl ester (6, 15, 16), glycerol trioleate (17), vitamin A acetate (6), acetone (1,3,5), 2-butanone (5), (cyclopentanone, 3-pentanone, cycloheptanone, 3-heptanone, cyclononanone) (18), 5-nonanone (18), cis-jasmone (6), phenylacetic acid (19), benzoic acid (13, 17), oleic acid (17), vanillin (19), benzaldehyde (5), phenol (14), m-cresol (8), benzyl ether (5), diethyl ether (5), caffeine (12,14), acridine (13), α-tocopherol (17), vitamin E, vitamin K1, vitamin K3) (6), limonene (6), indole (6), 1-octene (5), (dipentene, dichloromethane, chloroform) (5), hexachlorobenzene (9), (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane) (3), *n*-undecane (3), *n*-dodecane (3), *n*-tetradecane (3), 1,4-dioxane (5)
Solvent: ethylene	$Tr = 1.13$, $\rho_r = 1.86$–2.29, $N = 5$ 1 solute: naphthalene-d8 (11)
Solvent: ethane	$Tr = 1.01$–1.78, $\rho_r = 0.21$–1.96, $N = 28$ 2 solutes: 1-octene (20–22), 1-tetradecene (20)
Solvent: propane	$Tr = 1.04$–1.47, $\rho_r = 0.32$–2.03, $N = 32$ 3 solutes: benzene (8), m-cresol (8), 1-octene (22)
Solvent: *n*-hexane	$Tr = 1.00$–1.11, $\rho_r = 0.64$–1.97, $N = 66$ 7 solutes: (benzene, toluene, *p*-xylene, mesitylene, naphthalene, phenanthrene (23), 1-octene (22)
Solvent: 2,3-dimethylbutane	$Tr = 1.05$–1.10, $\rho_r = 1.43$–1.91, $N = 41$ 4 solues: (benzene, toluene, naphthalene, phenanthrene) (24)
Solvent: ethanol	$Tr = 1.00$–1.07, $\rho_r = 1.44$–2.06, $N = 55$ 5 solutes: (benzene, toluene, mesitylene, naphthalene, phenanthrene) (25)
Solvent: 2-propanol	$Tr = 1.00$–1.05, $\rho_r = 1.53$–2.08, $N = 48$ 6 solutes: (benzene, toluene, naphthalene, phenanthrene, *n*-decane, *n*-tetradecane) (26)
Solvent: chlorotrifluoromethane	$Tr = 1.04$–1.05, $\rho_r = 0.69$–1.72, $N = 30$ 3 solutes: (*p*-xylene, 1,3-dibromobenzene, acetone) (27)
Solvent: sulfur hexafluoride	$Tr = 1.01$–1.06, $\rho_r = 0.41$–1.91, $N = 68$ 5 solutes: (benzene, toluene, *p*-xylene, mesitylene, carbon tetrachloride (27)
Total: 107 binary systems	$Tr = 1.00$–1.78, $\rho_r = 0.21$–2.29, $\Sigma N = 1167$

*The data of Debenedetti and Reid (1986) and of Dahmen et al. (1990b) are omitted, as they are systematically low or high (Catchpole and King, 1994).

Cno:no = number of carbons, number of double bonds in fatty ester.

References in table:

(1) Sassiat et al. (1987); (2) Swaid and Schneider (1979); (3) Umezawa and Nagashima (1992); (4) Suarez et al. (1993); (5) Funazukuri (1996); (6) Funazukuri et al. (1992); (7) Olesik and Woodruff (1991); (8) Mei et al. (1995); (9) Akgerman et al. (1996); (10) Lauer (1983); (11) Lamb et al. (1989); (12) Knaff and Schlünder (1987); (13) Shenai et al. (1993); (14) Lai and Tan (1995); (15) Liong et al. (1992); (16) Funazukuri et al. (1991); (17) Catchpole and King (1994); (18) Dahmen et al. (1990a); (19) Wells et al. (1992); (20) Noel et al. (1994); (21) Eaton et al. (1995); (22) Eaton and Akgerman (1997); (23) Sun and Chen (1985a); (24) Sun and Chen (1985b); (25) Sun and Chen (1986); (26) Sun and Chen (1987); (27) Kopner et al. (1987).

$$AAD\% = \frac{100}{N}\sum_{i=1}^{N}|(D_{exp} - D_{pred})/D_{exp}| \quad (11)$$

Table 2 shows the typical results predicted by this work. For comparison, Table 2 also shows the results predicted by the Eaton and Akgerman method (Eaton and Akgerman, 1997), which is expressed as

$$D_{21} = \beta\sqrt{T}(\sigma_2/\sigma_1)^{\gamma}\left[\frac{m_1+m_2}{m_1m_2}\right]^{1/2}(V_0/\sigma_{21}^2)[(V_1/V_0)^{\alpha} - b_2] \quad (12)$$

where β is a constant related to its unit and $\gamma = 1.7538$ and

$$\sigma = (0.552803 - 0.0026776T_r)[6V_c/(\pi N_A)]^{1/3} \quad (13)$$

$$\alpha = \sigma_1/\sigma_2 - 1/3 \quad (14)$$

$$b_2 = \left[-0.2440(\sigma_1/\sigma_2)^2 + 0.8491(\sigma_1/\sigma_2) + 0.6001\right] \times (m_2/m_1)^{-0.03587} \quad (15)$$

As can be seen in Table 2, this work (Eqs. 10, 7 and 8) usually does well for predicting the diffusion coefficients of liquid and solid solutes in supercritical solvents, with a large density range ($\rho_r \geq 0.21$). Compared with the Eaton and Akgerman method (Eaton and Akgerman, 1997), this work has the merits of better prediction results and less input data.

Conclusions

The proposed correlations (Eqs. 10, 7 and 8) have been shown to successfully predict the binary infinite-dilution diffusion coefficients of liquid and solid solutes in supercritical solvents, with a large density range $\rho_r \geq 0.21$. The average absolute error of the predictions for 107 systems and 1,167 data points is 7.5%.

Table 2. Prediction Results for Infinite-Dilution Diffusion Coefficients of Liquid and Solid Solutes in Supercritical Solvents

					This Work AAD	This Work Max.	Eq. 12 AAD*	
Solvent	Solute	N	T_r	ρ_r	%	%	%	Citations
Carbon dioxide	benzene	69	1.00–1.10	0.60–2.00	8.0	23.4	6.0	1–7
	napthalene	75	0.95–1.10*	0.85–2.23	10.0	26.1	12.4	1,5,6,9–12
	phenanthrene	27	1.00–1.10	0.85–1.92	12.1	22.3	14.9	1,9,13
	C4:0 ethyl ester	16	1.01–1.05	1.28–1.82	2.7	7.3	11.0	15
	C14:0 ethyl ester	16	1.01–1.05	1.28–1.82	2.8	6.3	11.7	15
	C22:0 ethyl ester	17	1.01–1.05	1.28–1.82	2.2	4.8	20.4	15
	ethylacetate	15	1.01–1.08	0.45–1.72	7.4	14.3	/	14
	n-heptane	5	0.98–1.01	1.53–1.65	13.0	19.1	/	3
	toluene	18	1.01–1.08	0.46–1.72	5.6	12.3	/	14
	ethylbenzene	15	1.03–1.10	1.30–2.00	4.3	6.1	8.9	4
	phenol	21	1.01–1.08	0.76–1.72	3.8	9.8	/	14
	caffeine	21	1.01–1.08	0.91–1.72	6.9	25.4	/	14
	acetone	7	1.00–1.10	1.09–1.88	4.0	8.4	5.3	1
	cyclononanone	8	1.03	1.27–1.73	6.9	11.9	/	18
	phenylacetic acid	16	1.01–1.05	1.50–1.82	2.8	5.3	5.8	19
	vanillin	15	1.01–1.05	1.50–1.82	3.5	10.8	9.1	19
Ethylene	naphthalene-d8	5	1.13	1.86–2.29	4.3	8.3	/	11
Ethane	1-tetradecene	9	0.96–1.06*	1.52–1.77	7.2	15.1	7.7	20
	1-octene	13	1.71–1.78	0.21–0.55	13.8	27.4	/	21
Propane	benzene	12	1.04–1.09	1.47–2.03	11.0	24.3	/	7
n-hexane	benzene	12	0.93–1.07*	1.35–1.97	5.0	14.5	19.4	23
	naphthalene	13	0.83–1.07*	1.35–2.24	6.4	25.1	6.1	23
2,3-dimethylbutane	benzene	11	1.05–1.10	1.43–1.91	4.0	8.6	21.1	24
	naphthalene	9	1.05–1.10	1.43–1.91	4.4	6.7	7.5	24
Ethanol	benzene	13	0.92–1.07*	1.44–2.06	3.9	22.3	11.7	25
	naphthalene	13	0.92–1.07*	1.44–2.06	5.0	21.0	15.9	25
2-propanol	toluene	10	0.93–1.05*	1.53–2.08	7.9	15.1	8.2	26
	n-decane	10	0.93–1.05*	1.53–2.08	6.1	24.1	10.5	26
Chlorotrifluoro-methane	dibromobenzene	12	1.05	0.69–1.72	9.3	20.7	40.8	27
	acetone	10	1.04	0.69–1.65	8.0	23.6	40.4	27
Sulfur hexafluoride	mesitylene	11	1.03	0.41–1.91	9.0	22.4	18.7	27
	CCl_4	7	1.03	0.41–1.91	16.9	35.1	28.8	27
	Total	531			7.1%			

*Results quoted from Eaton and Akgerman (1997).
†For comparison with the Eaton and Akgerman method (Eaton and Akgerman, 1997), Eqs. 10, 7 and 8 are extended to the subcritical region.
References are the same as those in Table 1.

Notation

D = molecular diffusion coefficient, m^2/s
n = number density
N = number of data points
P = pressure, bar
V = molar volume (= 1,000 M/ρ), cm^3/mol
σ = diameter

Subscripts

1 = solvent
2 = solute
c = critical
E = Enskog

Literature Cited

Akgerman, A., C. Erkey, and M. Orejuela, "Limiting Diffusion Coefficients of Heavy Molecular Weight Organic Contaminants in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **35**, 911 (1996).

Catchpole, O. J., and M. B. King, "Measurement and Correlation of Binary Diffusion Coefficients in Near Critical Fluids," *Ind. Eng. Chem. Res.*, **33**, 1828 (1994).

Dahmen, N., A. Dülberg, and G. M. Schneider, "Determination of Binary Diffusion Coefficients in Supercritical Carbon Dioxide with Supercritical Fluid Chromatography (SFC)," *Ber. Bunsenges. Phys. Chem.*, **94**, 384 and 710 (1990a).

Dahmen, N., A. Kordikowski, G. M. Schneider, "Determination of Binary Diffusion Coefficients of Organic Compounds in Supercritical Carbon Dioxide by Supercritical Fluid Chromatography," *J. Chromatog.*, **505**, 169 (1990b).

Debenedetti, P. G., and R. C. Reid, "Diffusion and Mass Transfer in Supercritical Fluids," *AIChE J.*, **32**, 2034 (1986).

Dymond, J. H., "Hard-Sphere Theories of Transport Properties," *Chem. Soc. Rev.*, **3**, 317 (1985).

Easteal, A. J., and L. A. Woolf, "Diffusion in Mixtures of Hard Spheres at Liquid Densities: A Comparison of Molecular Dynamics and Experimental Data in Equimolar Systems," *Chem. Phys.*, **88**, 101 (1984).

Easteal, A. J., and L. A. Woolf, "Tracer Diffusion in Hard-Sphere Liquids from Molecular Dynamics Simulations," *Chem. Phys. Lett.*, **167**, 329 (1990).

Eaton, A. P., and A. Akgerman, "Infinite-Dilution Diffusion Coefficients in Supercritical Fluids," *Ind. Eng. Chem. Res.*, **36**, 923 (1997).

Eaton, A. P., D. B. Bukur, and A. Akgerman, "Molecular Diffusion Coefficients and Effective Diffusivities of 1-Octene in Supercritical Ethane in Relation to Fischer-Tropsch Synthesis," *J. Chem. Eng. Data*, **40**, 1293 (1995).

Funazukuri, T., S. Hachisu, and N. Wakao, "Measurement of Binary Diffusion Coefficients of C_{16}-C_{24} Unsaturated Fatty Acid Methyl Esters in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **30**, 1323 (1991).

Funazukuri, T., Y. Ishiwata, and N. Wakao, "Predictive Correlation for Binary Diffusion Coefficients in Dense Carbon Dioxide," *AIChE J.*, **38**, 1761 (1992).

Funazukuri, T., " Measurements of Binary Diffusion Coefficients of 20 Organic Compounds in CO_2 at 313.2 K and 16 MPa," *J. Chem. Eng. Japan*, **29**, 191 (1996).

Knaff, G., and E. U. Schlünder, "Diffusion Coefficients of Naphthalene and Caffeine in Supercritical Carbon Dioxide," *Chem. Eng. Process*, **21**, 101 (1987).

Kopner, A., A. Hamm, J. Ellert, R. Feist, and G. M. Schneider, "Determination of Binary Diffusion Coefficients in Supercritical Chlorotrifluoromethane and Sulphurhexafluoride with Supercritical Fluid Chromatography (SFC)," *Chem. Eng. Sci.*, **42**, 2213 (1987).

Lai, C. C., and C. S. Tan, "Measurement of Molecular Diffusion Coefficients in Supercritical Carbon Dioxide Using a Coated Capillary Column," *Ind. Eng. Chem. Res.*, **34**, 674 (1995).

Lamb, D. M., S. T. Adamy, K. W. Woo, and J. Jonas, "Transport and Relaxation of Naphthalene in Supercritical Fluids," *J. Phys. Chem.*, **93**, 5002 (1989).

Lauer, H. H., D. McManigill, and R. D. Board, "Mobile-Phase Transport Properties of Liquefied Gases in Near-Critical and Supercritical Fluid Chromatography," *Anal. Chem.*, **55**, 1370 (1983).

Liong, K. K., P. A. Wells, and N. R. Foster, "Diffusion of Fatty Acid Esters in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **31**, 390 (1992).

Liu, H. Q., C. M. Silva, and E. A. Macedo, "New Equations for Tracer Diffusion Coefficients of Solutes in Supercritical and Liquid Solvents Based on the Lennard-Jones Fluid Model," *Ind. Eng. Chem. Res.*, **36**, 246 (1997).

Mei, D. H., H. Q. Liu, and W. C. Wang, "Measurement and Correlation of Diffusion Coefficients for Alcohols in Supercritical CO_2," *J. Chem. Ind. Eng. (China)*, **46**, 357 (1995).

Noel, J. M., C. Erkey, D. B. Bukur, and A. Akgerman, "Infinite Dilution Mutual Diffusion Coefficients of 1-Octene and 1-Tetradecene in Near-Critical Ethane and Propane," *J. Chem. Eng. Data*, **39**, 920 (1994).

Olesik, S. V., and J. L. Woodruff, "Liquid Mass Transport Theories Applied to Molecular Diffusion in Binary and Ternary Supercritical Fluid Mixtures," *Anal. Chem.*, **63**, 670 (1991).

Perry, R. H., *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw Hill, New York, p. 3–270 (1984).

Sassiat, P. R., P. Mourier, M. H. Caude, and R. H. Rosset, "Measurement of Diffusion Coefficients in Supercritical Carbon Dioxide and Correlation with the Equation of Wilke and Chang," *Anal. Chem.*, **59**, 1164 (1987).

Shenai, V. M., B. L. Hamilton, and M. A. Matthews, "Diffusion in Liquid and Supercritical Fluid Mixtures," *Supercritical Fluid Engineering Science: Fundamentals and Applications*, E. Kiran and J. F. Brennecke, eds., Amer. Chem. Soc., Washington, DC, p. 92 (1993).

Suarez, J. J., J. L. Bueno, and I. Medina, "Determination of Binary Diffusion Coefficients of Benzene and Derivatives in Supercritical Carbon Dioxide," *Chem. Eng. Sci.*, **48**, 2419 (1993).

Sun, C. K. J., and S. H. Chen, "Tracer Diffusion of Aromatic Hydrocarbons in *n*-Hexane up to the Supercritical Region," *Chem. Eng. Sci.*, **40**, 2217 (1985a).

Sun, C. K. J., and S. H. Chen, "Diffusion of Benzene, Toluene, Naphthalene, and Phenanthrene in Supercritical Dense 2,3-Dimethylbutane," *AIChE J.*, **31**, 1904 (1985b).

Sun, C. K. J., and S. H. Chen, "Tracer Diffusion in Dense Ethanol: A Generalized Correlation for Nonpolar and Hydrogen-Bonded Solvents," *AIChE J.*, **32**, 1367 (1986).

Sun, C. K. J., and S. H. Chen, "Tracer Diffusion in Dense Methanol and 2-Propanol up to Supercritical Region: Understanding of Solvent Molecular Association and Development of an Empirical Correlation," *Ind. Eng. Chem. Res.*, **26**, 815 (1987).

Swaid, I., and G. M. Schneider, "Determination of Binary Diffusion Coefficients of Benzene and Some Alkylbenzenes in Supercritical CO_2 between 308 and 328 K in the Pressure Range 80 to 160 Bar with Supercritical Fluid Chromatography (SFC)," *Ber. Bunsenges. Phys. Chem.*, **83**, 969 (1979).

Umezawa, S., and A. Nagashima, "Measurement of the Diffusion Coefficients of Acetone, Benzene, and Alkane in Supercritical CO_2 by the Taylor Dispersion Method," *J. Superc. Fluids*, **5**, 242 (1992).

Wells, T., N. R. Foster, and R. P. Chaplin, "Diffusion of Phenylacetic Acid and Vanillin in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **31**, 927 (1992).

Manuscript received Feb. 24, 1997, and revision received July 11, 1997.