Diffusion Coefficients of Ethers in Supercritical Carbon Dioxide

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The Taylor−Aris tracer response method was applied to measure binary diffusion coefficients, D_{12}, in supercritical carbon dioxide under quasi-infinite-dilution conditions, by means of the Giddings and Seager chromatographic technique. Diethyl ether, diisopropyl ether, and tetrahydrofuran have been studied at 40, 50, and 60 °C in the pressure range 80−160 atm. The resulting binary diffusion coefficients are on the order of 10^{-4} cm^2/s. The influence of molecular weight, temperature, pressure, carbon dioxide density, and viscosity on the D_{12} values is extensively examined. The applicability of the Wilke−Chang and Tyn−Calus hydrodynamic correlations, the free-volume diffusion model of Dymond, the Catchpole and King correlation, and the Lennard-Jones model of Liu−Silva−Macedo is also evaluated.

Introduction

In the design and scale-up of supercritical processes, thermodynamic and transport properties are both relevant. Up until now, most studies on supercritical fluids (SCFs) are limited to the collection of vapor−liquid equilibrium data or to the measurement of solubilities of solutes in supercritical solvents. Mass-transfer studies are still scarce.

In many reviews of SCFs (Paulaitis et al., 1983; Johnston, 1983; Brenneck and Eckert, 1989; Vesovic and Wakcham, 1991; Liong et al., 1991), it is evidenced that there is a great lack of experimental diffusion data. Consequently, the number of theoretical- or empirical-based models describing diffusion is very reduced.

In recent years, there has been increasing interest in the experimental determination of these properties for different solutes in SCFs, especially CO_2. Nonetheless, there are still a great number of systems for which there are no available diffusivity data.

In this work binary diffusion coefficients for diethyl ether, diisopropyl ether, and tetrahydrofuran in supercritical carbon dioxide were measured using the chromatographic peak broadening (CPB) technique. The apparatus used was a supercritical chromatograph at 40, 50, and 60 °C in the pressure range 80−160 atm.

The experimental data are compared with predictions accomplished with the Wilke−Chang and Tyn−Calus semiempirical correlations, the Dymond free-volume-type expression, the Catchpole−King correlation, and the Liu−Silva−Macedo equation.

Theoretical Background

The chromatographic peak broadening technique is based on the fundamental work of Taylor (1953, 1954a,b), later extended by Aris (1956), which involved the dispersion of a solute in a laminar steady-state flow of mobile phase through a tube of uniform diameter. This simple technique was first used to measure diffusion coefficients of gaseous mixtures at low pressures by Giddings and Seager (1960), Bohemen and Purnell (1961), and other workers in the early 1960s. Since then, the CPB method has been extended to dense gases (Balenovic et al., 1970), to liquid systems (Ouano, 1972), and more recently to supercritical fluids (Feist and Schneider, 1982; Funazukuri et al., 1989).

In the Taylor dispersion method, a sharp pulse of a solute is introduced into a fully developed Poiseuille flow of a carrier fluid through an open straight column with a circular cross section. The injected peak will broaden due to the combined action of convection parallel to the axis and the molecular diffusion in the radial direction (in this application the axial dispersion is always negligible). If mutual diffusion was insignificant, the pulse would assume the parabolic profile, recording with a detector further down the tube a widely dispersed peak. In the case of very large mutual diffusivities, each molecule of the injected plug would sample all different streamlines in a short time and therefore would move with the average speed. In this case, the recorded peak downstream would repeat the original sharp one at the input. Thus, the broadening of the injected peak is a measure of the mutual diffusion coefficient, with a broad peak indicating a low diffusivity. The mathematical description of the concentration profile at the end of the column, in terms of a peak variance in units of length, is

$$\sigma^2(x) = \frac{2D_{12}L}{U_0} + \frac{R_0^{\,2}U_0L}{24D_{12}} = LH \tag{1}$$

where D_{12} is the binary molecular diffusivity, U_0 is the average linear velocity, R_0 and L are the inner radius and length of the column, respectively, and H is the so-called theoretical plate height. The axial diffusion term was ignored, due to the large longitudinal Peclet numbers, which measure the time ratio for diffusion and convection ($Pe_x = U_0L/D_{12}$).

Levenspiel and Smith (1957) showed that the concentration profile resulting from the dispersion of the pulse becomes essentially Gaussian, if the following condition applies:

$$D/U_0L < 0.01 \tag{2}$$

In this inequality D represents a dispersion coefficient which combines the effects of the parabolic axial profile

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and the effects of the radial molecular diffusion, according to $D = D_{12} + R_0^2U_0^2/48D_{12}$.

Equations 1 and 2 were specifically derived for the case of straight tubes. Nevertheless, due to the quite long lengths of tubing required for typical diffusion experiments, the tubing has to be coiled in order to be placed in a constant-temperature oven or bath. In such cases the velocity profile is elongated and there exists a secondary circulatory motion in the cross section, developed due to centrifugal forces (Jones, 1968). The deviation from the Taylor–Aris model caused by tube coiling is a function of the Reynolds group (*Re*), the Schmidt group (*Sc*), and the curvature ratio $\lambda = R_c/R_0$, where R_c is the tubing coil radius. It has been shown that under certain conditions *Re* and λ are not independent variables; the combination $Re/\sqrt{\lambda}$ determines the dispersion behavior instead. This combination is called Dean group (*De*) and expresses the relation between centrifugal forces and inertial forces.

According to Moulijn et al. (1977) and Alizadeh et al. (1980), the secondary flow effects can be neglected for high values of the curvature ratio, provided that the following restriction is adhered to:

$$De\sqrt{Sc} < 10 \qquad (3)$$

van der Laan (1958) states that if

$$U_0L/D > 1000 \qquad (4)$$

the perturbations due to temperature/pressure reduction occurring within a short length between the dispersion column and detector are negligible.

If the constraints imposed by eqs 2–4 are fulfilled, the diffusion coefficient can be directly determined from eq 1 after rearrangement:

$$D_{12} = \frac{U_0}{4}\left[H \pm \sqrt{H^2 - \frac{R_0^2}{3}}\right] \qquad (5)$$

Of the two possible values of D_{12}, only one is meaningful. Giddings and Seager (1962) showed that the negative root of the above equation has physical significance when the fluid velocity is greater than the optimal velocity, $U_{opt} = \sqrt{48}(D_{12}/R_0)$, which minimizes *H*. For velocities up to U_{opt}, the positive root should be used. Once the optimal velocity is normally very small for liquid and SCF systems, and hence easily exceeded, the negative sign is used in this work.

The theoretical plate height may be assessed by first measuring the half-width in time units at 0.607 of the peak height, $W_{0.607}$, and then calculating via the following expression:

$$H = \frac{U_0^2 W_{0.607}^2}{L} \qquad (6)$$

Experimental Section

Chemicals. *Solutes:* diethyl ether (Merck, extra pure, special for gas chromatography, minimum purity 99.5%), diisopropyl ether (BDH, special for HPLC, minimum purity 99.7%), tetrahydrofuran (Merck, extra pure, special for gas chromatography, minimum purity 99.5%). *Gases* (supplier, GASIN): hydrogen (purity 99.9995%), air (purity 99.995%), carbon dioxide (purity 99.9999%; aluminum cylinder with dip tube and helium head pressure).

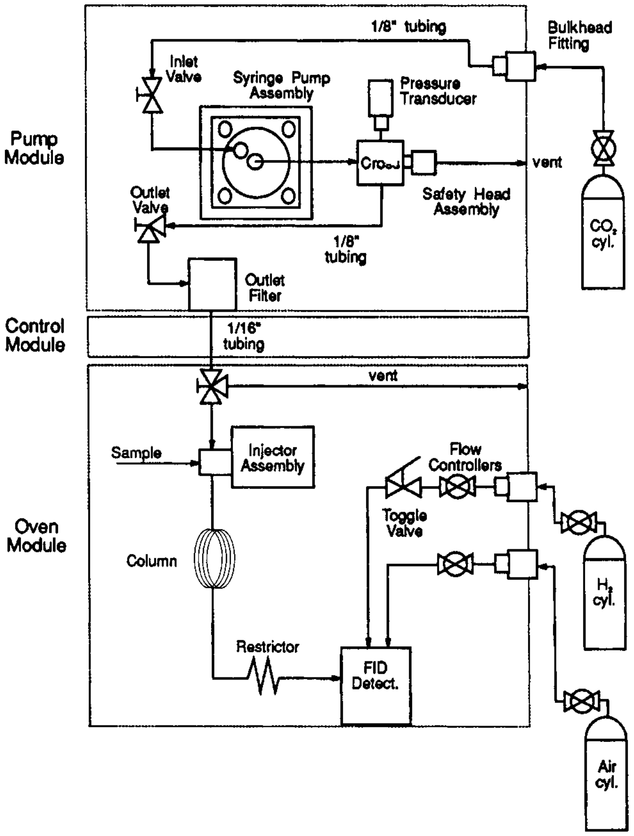

Figure 1. Scheme of the experimental device.

Equipment and Procedure. For the present research the experimental apparatus used is a commercially available supercritical fluid chromatograph, SUPREX 200A, equipped with additional instruments. The maximum pressure and temperature are 500 bar and 400 °C, respectively. The lower limits of 74 bar and 32 °C are introduced by the thermodynamic characteristics of carbon dioxide (i.e., the critical point: $P_c = 73.8$ bar and $T_c = 30.95$ °C). A schematic representation of the apparatus is given in Figure 1.

The experimental apparatus consists of three modules: the system for pumping and delivery of the solvent as supercritical fluid at the desired pressure, the oven where the diffusion capillary columns are kept at constant temperature, and a gas flame ionization detector (FID).

The solvent, carbon dioxide, is carried by a tube from the standard cylinder to the 250-mL syringe pump, where the pressure is raised to the specified value. After pressurization, the CO_2 is heated to the desired temperature, in the oven, where it flows through the column. The solute is injected into the solvent stream with a high-pressure valve (Rheodyne) equipped with a 0.2-μL loop. A gas FID is employed at the column exit to give the response signal. As is specific for gases, a restrictor is located between the column and the detector. It simultaneously maintains the solvent as a SCF in the column and controls the flow. The restrictor used in this work was a fused silica capillary tube with an inner diameter of 30 μm. The data from the detector are processed by using computer programs in C language developed for this purpose.

After the system temperature and pressure had reached the desired values, the flow system was allowed

Table 1. Experimental Conditions and Binary Diffusion Coefficients for Diethyl Ether, Diisopropyl Ether, and Tetrahydrofuran in Supercritical CO_2

temperature (K)	pressure (atm)	density[a] (g/cm^3)	viscosity[b] (10^{-4} g/cm·s)	diffusion coefficients (10^{-4} cm^2/s)		
				diethyl ether	diisopropyl ether	tetrahydrofuran
313.15	80	0.2919	2.327	3.255	2.961	3.723
313.15	100	0.6394	4.932	2.069	1.663	2.110
313.15	120	0.7235	5.998	1.571	1.426	1.741
313.15	140	0.7677	6.662	1.406	1.225	1.561
313.15	160	0.7987	7.181	1.391	1.182	1.417
323.15	80	0.2252	2.112	3.910	3.730	4.608
323.15	100	0.4017	2.952	2.812	2.651	3.182
323.15	120	0.5963	4.500	1.935	1.823	2.125
323.15	140	0.6793	5.434	1.751	1.706	1.788
323.15	160	0.7274	6.076	1.584	1.379	1.687
333.15	80	0.1960	2.064	4.998	4.897	5.235
333.15	100	0.2982	2.454	3.228	3.500	3.573
333.15	120	0.4479	3.296	2.410	2.406	2.708
333.15	140	0.5719	4.298	1.900	2.057	2.006
333.15	160	0.6450	5.056	1.831	1.529	1.981

[a] Calculated with the empirical equations of Pitzer and Schreiber (1988). [b] Calculated with the empirical equations of Altunin and Sakhabetinov (1972).

to equilibrate for approximately 2 h. After equilibrium was established, the experimental measurements were started. The solute was injected into the carbon dioxide stream by means of the above-mentioned injection valve. At least four pulses of solute were injected onto the column per run, and they were spaced by 20-min intervals to avoid any overlap of peaks.

Sources of Error. One of the difficulties encountered with diffusion coefficient measurements is the influence of injection, detection, and connecting tube volumes. To counteract these adverse effects, a two-column subtraction method was used in which the difference between the variance of the peak obtained in a long column and the variance obtained in a short column was determined. Hence, duplicate runs were performed on two stainless steel columns of lengths 20.537 and 11.939 m and both with an inner diameter of 1.00 mm. Such variance corresponds to a peak that would have been developed in a column of intermediate length (20.537−11.939 = 8.598 m), but without interference of the referred deleterious effects. Accordingly, the results were calculated by using eq 5 with

$$H = \frac{\sigma^2(t)_{\mathrm{long}} - \sigma^2(t)_{\mathrm{short}}}{L_{\mathrm{long}} - L_{\mathrm{short}}} U_0^{\,2} \qquad (7)$$

This procedure resulted in a maximum correction of 2%, which indicates that the initial peak dispersion and dead volume were minimal.

Linear velocities of supercritical CO_2 between 0.3 and 0.5 cm/s were employed in the majority of the experimental runs, resulting in residence times of 1−2 h for the runs with the long column and approximately half that time for the short column. The pressure drop disturbs the measurements only when the variation of mobile phase density vs pressure is important, i.e., close to the critical point. The head losses along the longer column were generally less than 0.1 atm. This should not greatly influence the diffusion coefficients obtained.

In all experimental runs, laminar flow was obtained. The Reynolds numbers always ranged between 20 and 90. The Levenspiel and Smith (1957) criterium was always verified: in all our experiments $D/U_0L < 0.0005$, ensuring that the concentration profile resulting from the dispersion of the pulse is Gaussian. The secondary flow effects induced by the action of centrifugal forces were negligible, $6.0 < De\sqrt{Sc} < 8.0$.

Adsorption can give large errors particularly for polar compounds in the low-density range, where the solvent power of the CO_2 is reduced. As suggested by Wells et al. (1992), the extent of peak tailing was measured by means of an asymmetric factor, defined as the ratio between the peak half-widths at 0.1 peak height. According to, e.g., Sassiat et al. (1987) and Liong et al. (1991), peaks with asymmetric factors higher than 1.2−1.3 have been considered unsuitable for analysis and therefore were rejected for the calculations. Obviously, the mean residence time of the peaks always overlapped the space time (L/U_0).

Experimental Conditions. The experiments for the three different ethers were carried out at three temperatures, 40, 50, and 60 °C, and pressures of 80, 100, 120, 140, and 160 atm. The solvent conditions at which diffusion coefficients were obtained are listed in Table 1. Density values were determined from an empirical relationship (Pitzer and Schreiber, 1988), and viscosity values, from an empirical equation developed by Altunin and Sakhabetinov (1972).

Results and Discussion

The data obtained for the diffusion coefficients of diethyl ether, diisopropyl ether, and tetrahydrofuran in supercritical CO_2, together with the temperatures and pressures at which the results were obtained, are presented in Table 1. The experimental diffusivities ranged from 1.182×10^{-4} to 5.235×10^{-4} cm^2/s.

In Table 2 all data necessary for experimental and prediction calculations are listed.

Taking into account all referred values, it is possible to justify two theoretical assumptions previously introduced, by quickly estimating some orders of magnitude. Using the $O(x)$ notation, which means "of order x", it is found that $L = O(10^3)$ cm, $R_0 = O(10^{-2})$ cm, $U_0 = O(10^{-1})$ cm/s, and $D_{12} = O(10^{-4})$ cm^2/s. Thus, it follows that (i) $Pe_x = O(10^6)$, which legitimates neglecting axial dispersion in the column, and (ii) $U_{\mathrm{opt}} = O(10^{-2})$ cm/s, which implies taking the negative root in eq 5.

Influence of Molecular Weight. Even though the ethers have different structures, the diffusion coefficient decreases with increasing molecular weight. Hence, it is possible to order diffusivities at the same conditions as follows: D_{12}(diisopropyl ether) < D_{12}(diethyl ether) < D_{12}(tetrahydrofuran).

Table 2. Data for Pure Substances

property	CO_2	diethyl ether	diisopropyl ether	tetrahydro-furan
M (g/mol)	44.010	74.123	102.177	72.107
P_c (bar)	73.8	36.4	28.8	51.9
T_c (K)	304.1	466.7	500.3	540.1
V_c (cm^3/mol)	93.9	280	386	224
T_{eb} (K)	202.94[a]	307.6	341.7	338
V_{eb} (cm^3/mol)	33.28[b]	105.34[c]	149.01[c]	83.74[c]
σ^{LJ} (Å)	3.26192[d]	5.23105[e]	5.74891[e]	4.89719[e]
ϵ^{LJ}/k (K)	500.72[d]	361.22[e]	387.23[e]	418.04[e]
D_c (10^{-4} cm^2/s)	4.9369[f]			

[a] Average of the values estimated using the Joback method (Reid et al., 1988) and Guldberg's rule: $T_{eb} = (2/3)\ T_c$. [b] Estimated by the Tyn−Calus expression (Reid et al., 1988). [c] Average of the values estimated using the Le Bas method and the Tyn−Calus expression (Reid et al., 1988). [d] Values taken from Liu et al. (1998). [e] Parameters estimated according to Silva et al. (1998) (eqs B.5 and B.6). [f] Estimated by eq A.6 (Catchpole, 1991).

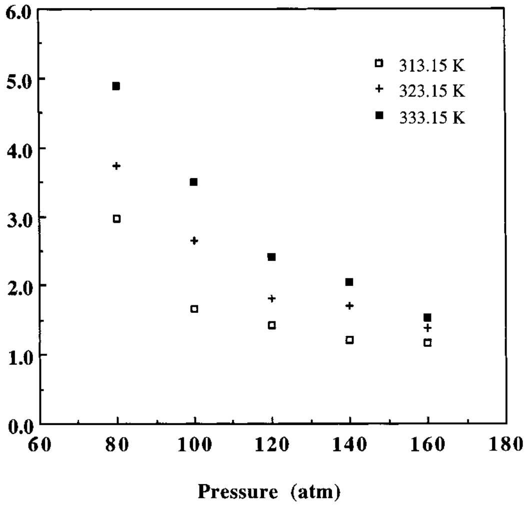

Figure 2. Diffusion coefficients of diisopropyl ether as a function of pressure at constant temperatures.

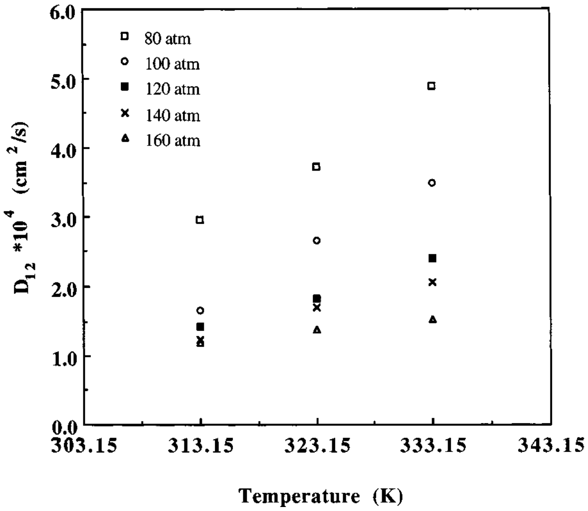

Figure 3. Diffusion coefficients of diisopropyl ether as a function of temperature at constant pressures.

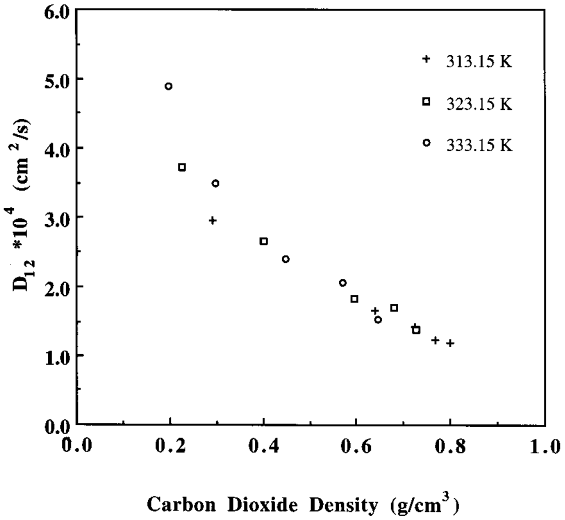

Figure 4. Diffusion coefficients of diisopropyl ether as a function of carbon dioxide density.

Influence of Pressure at Constant Temperature. The pressure dependence of the binary diffusion coefficient at constant temperature for the diisopropyl ether is shown in Figure 2. Similar behavior was found for diethyl ether and tetrahydrofuran. The general trend is that D_{12} decreases with increasing pressure, with this influence being less significant at higher pressures and varying with temperature, a trend reported in all previous studies. The greater pressure sensitivity of D_{12} at low pressures is probably linked to changes in solvent viscosity or density, both of which change rapidly with pressure in this region.

Influence of Temperature at Constant Pressure. Figure 3 represents D_{12} vs temperature at isobaric conditions for the diisopropyl ether. A similar trend was found for diethyl ether and tetrahydrofuran. From Figure 3 a high dependence of the diffusion coefficient at constant pressure is observed, according to previous investigations (e.g., Swaid and Schneider, 1979; Suárez et al., 1993). This behavior suggests that the pronounced temperature dependence may be due to the decrease in solvent density associated with the increase in system temperature.

Influence of Density at Constant Temperature. The relationship between the diffusion coefficients and density at constant temperature is illustrated, by way of the example for diisopropyl ether, in Figure 4. As was expected, a large dependence of D_{12} on density is observed. As the density rises, the path taken by the solute molecule through the solution becomes more erratic, resulting in a sharp decline in diffusivity. In fact, the molecular diameter becomes more significative in comparison with the average intermolecular distance, which increases both the collision transfer and the number of collisions per second (Hirschfelder et al., 1967). Figure 4 also points out that, at low densities, D_{12} values were found to be greater than predicted by extrapolating the linear relationship observed at high densities. Such divergence corroborates the results obtained by several authors (e.g., Sassiat et al., 1987; Wells et al., 1992).

Influence of the Stokes−Einstein Type. Figure 5 is a plot of the diisopropyl ether data in D_{12} vs $T\eta^{-1}$ coordinates. As can be seen, the plot is linear to a good approximation, but the finite nonzero intercept emerges deviation from hydrodynamic behavior ($D_{12} \propto T/\eta$). The results obtained for the three ethers are consistent with the trends found by previous researchers (e.g., Feist and Schneider, 1982; Debenedetti and Reid, 1986).

Modeling the Diffusion Data

Stokes−Einstein-Based Correlations. The hydrodynamic theory, based on the Stokes−Einstein relation-

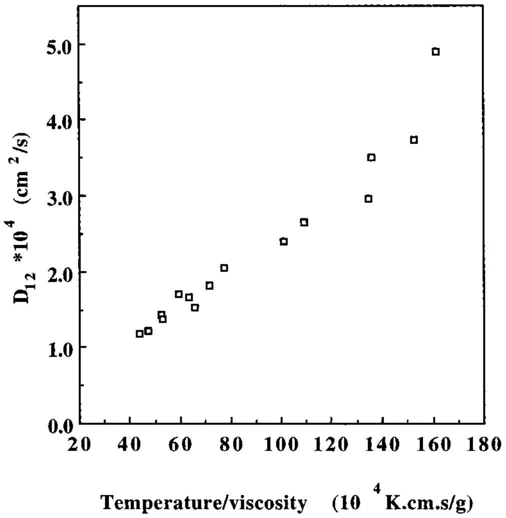

Figure 5. Diffusion coefficients of diisopropyl ether plotted in Stokes−Einstein fashion.

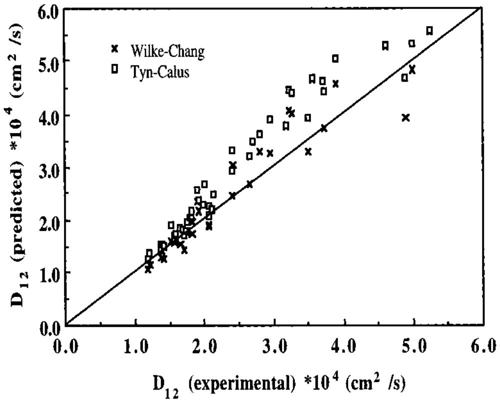

Figure 6. Comparison of the predictions of both the Wilke−Chang and Tyn−Calus correlations with all experimental data.

ship, was initially formulated for liquids and then extended to dense gases and supercritical systems.

In this work we applied the Wilke−Chang (WC) and Tyn−Calus (TC) estimation methods, eqs 8 and 9, respectively (Reid et al., 1988), to the three systems investigated.

$$D_{12} = 7.4 \times 10^{-8}\frac{(\phi M_1)^{1/2}T}{\eta_1 V_{2,\mathrm{eb}}^{\;0.6}} \tag{8}$$

$$D_{12} = 8.93 \times 10^{-8}\frac{V_1^{\;0.267}}{V_2^{\;0.433}}\left(\frac{\tau_{1,\mathrm{eb}}}{\tau_{2,\mathrm{eb}}}\right)^{0.15}\frac{T}{\eta_1} \tag{9}$$

The subscripts 1, 2, and eb stand for “solvent”, “solute”, and “normal boiling point”, respectively; M is the molecular weight in g/mol, T the temperature in K, η the viscosity in cP, V the molar volume in cm^3/mol, and τ the surface tension in g/cm·s^2. The molar volumes at normal boiling point were determined from the Le Bas group contribution technique (Reid et al., 1988) and/or the simple relation by Tyn and Calus (Reid et al., 1988). For the fictitious normal boiling temperature of carbon dioxide was taken the average of two results differing by 0.205% only, given by the Joback method and Guldberg’s rule ($T_{\mathrm{eb}} = (2/3)T_{\mathrm{c}}$) (Reid et al., 1988). The ratio of surface tensions was calculated by the Brock and Bird corresponding states method, also described in the excellent book of Reid et al. (1988).

Table 3 contains the absolute average deviations (AAD) for both models. Figure 6 shows the predicted diffusion values for the three ethers versus the experimental ones. Generally it was found that WC gave the best fit. The failure of the Stokes−Einstein-based equations is especially evident in regions of low CO$_2$ density (viscosity), where the compressibility is large. Here, the highly negative partial molar volumes readily observed (Foster et al., 1989; Eckert et al., 1986) reveal solvent clustering around solute molecules, which severely impedes solute diffusion. This finding corroborates earlier studies by several authors (e.g., Debenedetti and Reid, 1986; Wells et al., 1992).

Dymond Free-Volume Type Expression. Following the original work of Batschinski (1913) for real liquids, later reestablished by Hildbrand (1971), the diffusion of a solute at infinite dilution will obey an equation of the form

$$D_{12} = B'V_{\mathrm{f}} = B'(V_1 - V'_{\mathrm{D}}) \tag{10}$$

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_1 is the solvent molar volume. However, according to Ertl and Dullien (1973), eq 10 departs from the predicted linear relationship for the entire temperature range, leading them to introduce a third parameter, n, to increase the dependence of diffusivity on volume expansion: $D_{12} = B''(V_{\mathrm{f}})^n$.

The results obtained by Dymond (1974) for the self-diffusivity of hard spheres prompted Chen et al. (1982) to suggest that instead of eq 10 the preferred equation should be

$$D_{12} = B\sqrt{T}(V_1 - V_{\mathrm{D}}) \tag{11}$$

This model, henceforth called DHB (Dymond−Hildbrand−Batschinski), exhibits quite different V_{D}s for the same solvent and, sometimes, even negative values. Such physically meaningless results have been found in a previous work by Liu et al. (1997), for 13 of 46 supercritical systems studied (performing 734 experimental points). This work confirmed such inconsistencies, as different and negative V_{D} values were obtained (diethyl ether, −26.57 cm^3/mol; diisopropyl ether, −16.30 cm^3/mol; tetrahydrofuran, −22.15 cm^3/mol). Table 3 contains the AAD as well as the optimized B and V_{D} for the three ethers being studied. The low AADs presented (diethyl ether, 4.98%; diisopropyl ether, 7.87%; tetrahydrofuran, 4.99%), are mainly due to the number of parameters that have been regressed. Concerning interest about the DHB model, we emphasize that it is

Table 3. Calculation Results

solute	Wilke−Chang (AAD$_{\mathrm{WC}}$)	Tyn−Calus (AAD$_{\mathrm{TC}}$)	Dymond $B \times 10^7$	Dymond V_{D}	Dymond (AAD$_{\mathrm{DHB}}$)	Catchpole−King (AAD$_{\mathrm{CK}}$)	Liu−Silva−Macedo (AAD$_{\mathrm{TLSM}}$)
diethyl ether	11.55	19.98	1.0475	−26.57	4.98	28.33	16.97
diisopropyl ether	7.46	14.12	1.0782	−16.30	7.87	15.49	14.80
tetrahydrofuran	15.19	15.72	1.1872	−22.15	4.99	28.52	14.87

confined to correlative purposes only. 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).

Catchpole−King Correlation. Recently, Catchpole and King (1994) devised a new prediction correlation for near-critical fluids:

$$D_{12} = 5.152 D_{1,\mathrm{c}} T_{\mathrm{r}} (\rho_{1,\mathrm{r}}{}^{-2/3} - 0.4510) F/X \qquad (12)$$

In this equation ρ represents the density, $D_{1,\mathrm{c}}$ is the solvent self-diffusion coefficient at the critical point, F and X are correction factors, and the subscript r denotes reduced property. Appendix A contains a detailed description of the model, hereafter identified by CK, as well as all subsidiary equations necessary for the calculation.

In Table 3 are listed the results achieved with CK correlation for the ethers which are being studied in this essay. The large deviations found (diethyl ether, 28.33%; diisopropyl ether, 15.49%; tetrahydrofuran, 28.52%) may be due to the following points: (1) The diffusion coefficients may be liable to considerable errors, due to the large variance the F vs X fittings exhibit (see eqs A.3 and A.4). (2) Factor F depends upon the binary system, which for ethers is 1.0 according to CK criteria (Appendix A). Nonetheless, in their original work no calculations involving ethers have been made to justify this assumption. (3) The temperature (and density) dependence of the hard-sphere diameter was neglected. Nevertheless, it is well-known how large the effect of small changes in an assigned diameter can be on calculated transport coefficients (e.g., Liu et al., 1998).

Tracer Liu−Silva−Macedo Equation. The Lennard-Jones model of Liu−Silva−Macedo (TLSM) (Liu et al., 1997) was also adopted in this paper to predict the mutual diffusivities of the ethers in supercritical CO_2. In that model Liu and co-workers (Liu et al., 1997) chose the two-parameter equation they have developed previously for the self-diffusion coefficients (LSM) (Liu et al., 1998), which is summarily described in Appendix B.

The limiting mutual diffusion coefficients equation is as follows:

$$D_{12} = 21.16 \left(\frac{1000RT}{M_{12}} \right)^{1/2} \frac{V_1}{N_{\mathrm{a}} (\sigma_{12}^{\mathrm{eff}})^2} \times \exp\left(-\frac{0.75\rho_1^*}{1.2588 - \rho_1^*} - \frac{0.27862}{T_{12}^*} \right) \qquad (13)$$

where N_{a} is Avogadro's constant, R is the ideal gas constant, and the subscript 12 stands for "binary"; ρ_1^* is the reduced solvent density, defined by eq B.3; $\sigma_{12}^{\mathrm{eff}}$ and T_{12}^* are the effective hard-sphere diameter and the reduced temperature, which are still calculated by respectively eqs B.2 and B.4 but are presently defined in terms of the binary Lennard-Jones diameter and energy $\sigma_{12}^{\mathrm{LJ}}$ and $\epsilon_{12}^{\mathrm{LJ}}/k$. The reduced mass of the system, M_{12}, is

$$M_{12} = \frac{2 M_1 M_2}{M_1 + M_2} \qquad (14)$$

The energy and diameter combining rules used by the authors are

$$\epsilon_{12}^{\mathrm{LJ}}/k = \sqrt{(\sigma_1^{\mathrm{LJ}})^3 (\epsilon_1^{\mathrm{LJ}}/k)(\sigma_2^{\mathrm{LJ}})^3 (\epsilon_2^{\mathrm{LJ}}/k)}/(\sigma_{12}^{\mathrm{LJ}})^3 \qquad (15)$$

$$\sigma_{12}^{\mathrm{LJ}} = \frac{\sigma_1^{\mathrm{LJ}} + \sigma_2^{\mathrm{LJ}}}{2} \qquad (16)$$

Therefore, this is a purely predictive model. The only input data required are temperature, solvent density, and, for both components, molecular weight and the Lennard-Jones force constants (energy and diameter). For substances whose self-diffusivities have been correlated by the authors with eq B.1, the potential parameters may be taken from Liu et al. (1998). For other substances, the generalized equations provided by Silva et al. (1998) should be used to estimate them (eqs B.5 and B.6). In this work the Lennard-Jones constants of the three ethers had to be estimated (Table 2); the values for CO_2 were available.

The calculated results are presented in Table 3. It may be observed that the TLSM equation performs much better than the CK correlation, except for diisopropyl ether where the difference is smaller ($\mathrm{AAD}_{\mathrm{TLSM}} = 14.80\%$ and $\mathrm{AAD}_{\mathrm{CK}} = 15.49\%$). The prediction is also better than that achieved with TC correlation, except for diisopropyl ether ($\mathrm{AAD}_{\mathrm{TLSM}} = 14.80\%$ and $\mathrm{AAD}_{\mathrm{TC}} = 14.12\%$). With regard to the WC correlation, it is found that it exhibits lower deviations (5−7%) for diethyl and diisopropyl ethers; nonetheless, it behaves a little worse than the TLSM model for tetrahydrofuran ($\mathrm{AAD}_{\mathrm{TLSM}} = 14.87\%$ and $\mathrm{AAD}_{\mathrm{WC}} = 15.19\%$). Generally we may detach the reasonable performance of the TLSM model, once the Lennard-Jones diameters and interaction energies have been estimated. These being calculated by generalized expressions, we may expect this stopgap to introduce additional errors.

Conclusions

The binary diffusion coefficients of diethyl ether, diisopropyl ether, and tetrahydrofuran in supercritical carbon dioxide were determined at 40, 50, and 60 °C and pressures of 80, 100, 120, 140, and 160 atm (which means densities between 0.196 and 0.799 g/cm^3) by the chromatographic peak broadening technique. The experimental diffusivities obtained ranged from 1.182×10^{-4} up to 5.235×10^{-4} cm^2/s. It was observed that, at the same conditions, the diffusivities can be ordered as D_{12}(diisopropyl ether) < D_{12}(diethyl ether) < D_{12}(tetrahydrofuran).

The influence of temperature and pressure on the diffusion coefficients was found to be largely the result of consequent changes in the carbon dioxide density. The relationship between D_{12} and CO_2 density was observed to be linear except in regions of high CO_2 compressibility, where the experimental values are superior than the predicted ones by extrapolating the linear relationship.

Concerning prediction, we may say succinctly that the following apply: (1) Generally it was found that the Wilke−Chang correlation gives the best fit. The Tyn−Calus equation overpredicted significantly the diffusivities, especially in regions of low density. This behavior has been reported in previous studies. (2) The free-volume-based equation of Dymond provided good fittings, although it exhibits negative and quite different minimum free volumes for diffusion, as has been already found for other substances. Nonetheless, such good results are mainly due to the optimization of two parameters. (3) The Tracer Liu−Silva−Macedo model presented reliable results, notwithstanding the estimation of the energy and diameter parameters of the solute by generalized expressions. (4) The Catchpole−King correlation gave the worst prediction.

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Nomenclature

AAD = average absolute deviation, (100/NDP)$\sum_{i=1}^{\mathrm{NDP}}|D^{*\mathrm{cal}}_{12,i} - D^{*\mathrm{exp}}_{12,i}|/D^{*\mathrm{exp}}_{12,i}$
B = parameter in eqs 10 and 11
CK = Catchpole−King correlation for tracer diffusivities (Appendix A)
CPB = chromatoghaphic peak broadening technique
$D = D_{12} + R_0^2U_0^2/48D_{12}$ = dispersion coefficient, cm^2/s
D_1 = solvent self-diffusivity, cm^2/s
$D_{1,c}$ = solvent self-diffusion coefficient at the critical point, cm^2/s
D_{12} = limiting mutual diffusion coefficient, cm^2/s
$De = Re/\sqrt{\lambda}$ = Dean number
DHB = Dymond−Hildbrand−Batschinski (eq 11)
F = correction factor defined by eqs A.3 and A.4
FID = flame ionization detector
H = theoretical plate height, cm
L = column length, cm
LSM = Liu−Silva−Macedo model for self-diffusion coefficients (Appendix B)
M = molecular weight, g/mol
n = parameter in Ertl and Dullien modification of the DHB equation, $D_{12} = B''(V_f)^n$
N_a = Avogadro's constant
NDP = number of data points
P = pressure, bar or atm
$Pe_x = U_0L/D_{12}$ = longitudinal Peclet number
R = 8.3144 J/mol·K, gas constant
R_0 = inner radius of the column, cm
R_c = tubing coil radius, cm
$Re = 2R_0U_0\rho/\eta$ = Reynolds number
$Sc = \eta/\rho D_{12}$ = Schmidt number
SCF = supercritical fluid
T = temperature, K
TLSM = Liu−Silva−Macedo model for tracer diffusivities (eq 13)
U_0 = average linear velocity, cm/s
$U_{\mathrm{opt}} = \sqrt{48}(D_{12}/R_0)$ = optimal average linear velocity (which minimizes H), cm/s
V = molar volume, cm^3/mol
V_D = parameter in eqs 10 and 11, cm^3/mol
V_f = free volume, cm^3/mol
$W_{0.607}$ = half-width at 0.607 of the peak height, s
X = size to mass ratio parameter given by eq A.2

Greek Letters

ϵ/k = Lennard-Jones energy parameter, K
ϕ = association factor in eq 8
η = viscosity, g/cm·s or cP
$\lambda = R_c/R_0$ = curvature ratio
σ = Lennard-Jones molecular diameter, cm or Å
$\sigma^2(x)$ = peak variance, cm^2
Σ_v = diffusion volume in eq A.6
ρ = density, g/cm^3 or cm^{-3}
τ = surface tension, g/cm·s^2

Subscripts

1 = solvent
2 = solute
12 = binary property
c = critical property
eb = normal boiling point
r = reduced property

Superscripts

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

Appendix A: Catchpole−King Correlation

Catchpole and King (1994) developed a new prediction correlation for binary diffusion coefficients of near-critical fluids ($\rho_r \approx 1-2.5$ and $T_r \approx 0.9-1.3$), following the self-diffusivity correction procedure. Accordingly, the main expression is

$$D_{12} = 2^{3/2}D_1F/X \tag{A.1}$$

where D_1 is the solvent self-diffusivity, X is a size to mass ratio parameter given by

$$X = \frac{[1 + (V_{2,c}/V_{1,c})^{1/3}]^2}{\sqrt{1 + M_1/M_2}} \tag{A.2}$$

and F is a correction factor defined for two different classes of systems.

(i) *Class 1 Type System*. All aliphatics except ketones and (for ethylene) naphthalene in carbon dioxide and ethylene. In this case F is independent of the size to mass ratio parameter X and is correlated by

$$F = 1.0 \pm 0.1, \qquad 2 < X \tag{A.3}$$

(ii) *Class 2 Type System*. All aromatics, ketones, and carbon tetrachloride in carbon dioxide; all aromatics, (for $CClF_3$) 2-propanone, (for SF_6) carbon tetrachloride in propane, hexane, dimethylbutane, SF_6, and $CClF_3$. In this case a weak dependence on X is given:

$$F = 0.664X^{0.17} \pm 0.1, \qquad 2 < X < 10 \tag{A.4}$$

According to Catchpole et al. (1993), the original paper (Catchpole and King, 1994) has a mistake, since it lacks the head factor 0.664.

Taking account of the correlations of Dymond (1972) and Erkey et al. (1990) for D_1 and introducing a modification in their temperature dependence, the final binary coefficient has been obtained:

$$D_{12} = 5.152D_{1,c}T_{1,r}({\rho_{1,r}}^{-2/3} - 0.4510)F/X \tag{A.5}$$

The solvent self-diffusion coefficient at the critical point, $D_{1,c}$, is estimated from a modified Fuller−Schettler−Giddings (Fuller et al., 1966) empirical correlation to give D_1 in terms of the critical density (Catchpole, 1991)

$$D_{1,c} = \frac{4.300 \times 10^{-7}{M_1}^{1/2}{T_c}^{0.75}}{(\Sigma_{v,1})^{2/3}\rho_{1,c}} \tag{A.6}$$

with $\rho_{1,c}$ in kg/m^3 and the diffusion volumes, $\Sigma_{v,1}$, calculated according to Reid et al. (1988).

Appendix B: Liu−Silva−Macedo Equation

The Lennard-Jones model of Liu−Silva−Macedo (Liu et al., 1998) for self-diffusion coefficients, D_1, is

$$D_1 = 21.16\left(\frac{1000RT}{M_1}\right)^{1/2}\frac{V_1}{N_a(\sigma_1^{\mathrm{eff}})^2}\times \exp\left(-\frac{0.75\rho_1^*}{1.2588-\rho_1^*}-\frac{0.27862}{T_1^*}\right) \qquad \text{(B.1)}$$

where σ_1^{eff} is the effective hard-sphere diameter and ρ_1^* and T_1^* are the reduced density and temperature, respectively:

$$\sigma_1^{\mathrm{eff}} = 2^{1/6}\sigma_1^{\mathrm{LJ}}[1+(1.3229T_1^*)^{1/2}]^{-1/6} \qquad \text{(B.2)}$$

$$\rho_1^* = \rho_1(\sigma_1^{\mathrm{eff}})^3 = \frac{N_a}{V_1}(\sigma_1^{\mathrm{eff}})^3 \qquad \text{(B.3)}$$

$$T_1^* = \frac{T}{\epsilon_1^{\mathrm{LJ}}/k} \qquad \text{(B.4)}$$

Therefore, this model contains only two parameters: the pure component Lennard-Jones energy ($\epsilon_1^{\mathrm{LJ}}/k$, in K) and diameter ($\sigma_1^{\mathrm{LJ}}$, in cm). For substances whose self-diffusivities have been correlated with eq B.1, the molecular parameters are taken from Liu et al. (1998). For other substances, the generalized equations provided by Silva et al. (1998) should be used to estimate them:

$$\epsilon_1^{\mathrm{LJ}}/k = 0.774T_c \qquad \text{(B.5)}$$

$$\sigma_1^{\mathrm{LJ}} = 10^{-8}\left[0.17791 + 11.779\frac{T_c}{P_c} - 0.049029\left(\frac{T_c}{P_c}\right)^2\right]^{1/3} \qquad \text{(B.6)}$$

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