

**Diffusion of Benzyl Acetate, 2-Phenylethyl Acetate, 3-Phenylpropyl acetate
and Dibenzyl Ether in mixtures of carbon dioxide and ethanol**

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Abstract

Diffusion coefficients of four solutes at infinite dilution (benzyl acetate, 2-phenylethyl acetate, 3-phenylpropyl acetate and dibenzyl ether) were measured in the system CO₂+ethanol from 313.16 to 333.16 K and pressures between 15 and 35 MPa over the full concentration range of the CO₂+ethanol mixture. The diffusional behaviour in the mixed solvent was compared with the estimation of seven simple predictive equations, Le Blanc, Wilke-Chang, Holmes-Olander-Wilke, Tang-Himmelblau (two formulas), Perkins-Geankoplis, and Leffler-Cullinam, observing that the first two give errors between 17 and 30% and that deviations lower than 11% are only obtained with the expressions of Tang-Himmelblau. Nevertheless, as none of the studied equations considers the self-association of ethanol nor complex formation between solute and alcohol molecules, the model of Lusi-Ratcliff and Mohan-Srinivasan was extended to ternary liquid-supercritical systems with the diffusing component dilute, obtaining average absolute deviations lower than 4.6% for the diffusivities of the four solutes. Nevertheless, the extension of this model is correlative (it needs one adjustable parameter for each solute), not predictive.

1. Introduction

It is known that the addition of small quantities of organic solvents can greatly change the solubilities of substances in supercritical carbon dioxide.¹ These organic solvents, usually called “entrainers”, “cosolvents” or “modifiers” change the diffusion coefficients, and therefore the mass transfer processes can be accelerated or slowed down,^{2 - 4} which can be very interesting for industrial applications. Nevertheless, only a few experimental data for CO₂+entrainer systems are available, and there are lack of rigorous theoretical studies of the solute movility in such mixtures. Most efforts focuses on pure carbon dioxide.^{5 -12}

Funazukuri^{13, 14} and Olesik^{3, 15} employed the Wilke-Chang equation for estimating the diffusion coefficient of a dilute solute in a mixture of solvents (one of them being carbon dioxide) because this empirical correlation is very simple and only needs the viscosity of mixture, but there are more equations that could be applied to the systems CO₂+entrainer, although they needs more information that Wilke-Chang formula. For example, the equations of Holmes-Olander-Wilke, Perkins-Geankoplis, Tang-Himmelblau (all three are explained in refs 16 and 17) and Lefler-Cullinam.¹⁸ These are all based in the Eyring kinetic theory, and require the viscosities of pure compounds besides the limiting binary diffusivities of solute in each one. Another very simple equation is the Le Blanc formula,^{16, 17} which is based in Stefan-Maxwell expression and only require the two limiting binary diffusivities, but yields poor agreement with experimental results.

In the present research, experimental diffusion coefficients of benzyl acetate, 2-phenylethyl acetate, 3-phenylpropyl acetate and dibenzyl ether at infinite dilution in the ternary systems solute+CO₂+ethanol were measured at eight mass fractions of ethanol (including pure CO₂ and pure alcohol). The four solutes were selected because of their importance as ingredients of fragrances, and the ethyl alcohol was chosen as the entrainer instead of methanol (the most widely used cosolvent,^{2, 4, 19, 20}) because it is innocuous, and can be a better modifier in the pharmaceutical or food industries. As the minimum pressure is 15 MPa, the Taylor-Aris chromatographic broadening technique was used. The experimental data are compared with the above-mentioned equations, but since alcohols forms hydrogen bonds with themselves and with esters and ethers, these formulas will probably not be able to produce good predictions.

The fundamental law of diffusion, the Fick's law, can be modified to take into account the association effects through mass balances and chemical equilibrium constants.^{21, 22} Alcohol polymerization and solute-solvent complexation are supposed to be like chemical reactions, and the ternary system becomes a multicomponent solution, where monomers, oligomers, polymers and all type of complexes diffuse.

2. Theoretical approach

2.1. Predictive Models for Diffusion in Mixed Solvents. Wilke²³ developed from the Stefan-Maxwell equation the following formula for the diffusion of one component i in the mixture of m gases at low pressure (denoted by the superscript 0)

$$D_{im}^0 = \frac{1 - x_i}{\sum_{j=2}^m \frac{x_j}{D_{ij}^0}} \quad (1)$$

When $m=3$ and the solute mole fraction is very low ($x_i \rightarrow 0.0$), this formula can be reduced to the Le Blanc expression,¹⁶ whose predictions in liquid can deviate to 30% from experimental results specially in low viscosity mixtures.

$$D_{1m}^\infty = \frac{1}{\frac{x_2}{D_{12}^\infty} + \frac{x_3}{D_{13}^\infty}} \quad (2)$$

In eq 2 the low-pressure diffusivities have been replaced by the limiting diffusion coefficient of the solute in each solvent D_{1j}^∞ .

The modified Wilke-Chang equation is²⁴

$$D_{1m}^\infty = \frac{5.88 \times 10^{-17} T \sqrt{\sum_{j=2}^m (x_j M_j f_j)}}{\eta_m V_{b1}^{0.6}} \quad (3)$$

where M is the molar mass, V_b the molar volume at normal boiling point, η the viscosity and f an adimensional association factor (2.6 if the solvent is water, 1.9 if it is methanol, 1.5 if it is ethanol and 1.0 if it is unassociated). This correlation overestimates the diffusivities of m -cresol and benzene in supercritical mixtures of acetonitrile+CO₂ and H₂O+propane.³ When benzene derivatives move in the ternary solvent ethanol+CO₂+H₂O, Souvignet and Olesik¹⁵

indicate that the predicted values for anthracene and benzene are smaller than experimental ones but are reasonably good for *m*-cresol and 3-nitrophenol, which is strange because the interactions between these substances and water and ethanol.

From the Eyring kinetic theory there are four equations: ¹⁶⁻¹⁸

a) Holmes-Olander-Wilke

$$D_{1m}^{\infty} \eta_m = x_2 D_{12}^{\infty} \eta_2 + x_3 D_{13}^{\infty} \eta_3 \quad (4)$$

b) Tang-Himmelblau I

$$D_{1m}^{\infty} \eta_m^{1/2} = x_2 D_{12}^{\infty} \eta_2^{1/2} + x_3 D_{13}^{\infty} \eta_3^{1/2} \quad (5)$$

c) Tang-Himmelblau II

$$\ln(D_{1m}^{\infty} \eta_m^{1/2}) = x_2 \ln(D_{12}^{\infty} \eta_2^{1/2}) + x_3 \ln(D_{13}^{\infty} \eta_3^{1/2}) \quad (6)$$

d) Perkins-Geankoplis

$$D_{1m}^{\infty} \eta_m^{0.8} = x_2 D_{12}^{\infty} \eta_2^{0.8} + x_3 D_{13}^{\infty} \eta_3^{0.8} \quad (7)$$

e) Leffler-Cullinan

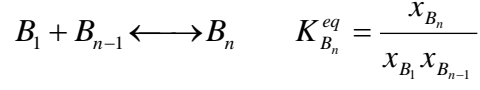
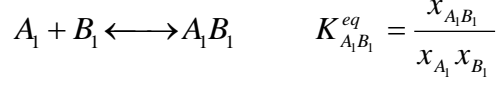
$$\ln(D_{1m}^{\infty} \eta_m) = x_2 \ln(D_{12}^{\infty} \eta_2) + x_3 \ln(D_{13}^{\infty} \eta_3) \quad (8)$$

The two formulas of Tang-Himmelblau give good predictions for the diffusion of toluene in alkane+alkane and alkane+cycloalkane mixtures, and for CO₂ in benzene+toluene, CCl₄+toluene and ethanol+water. For these systems, and dilute acetic acid in aqueous ethanol

and KCl in aqueous glycol, the Perkins-Geankoplis expression was empirically developed from eqs 4 and 5. The Lefler-Cullinam equation has deviations of 2-5% for the nine possible situations of the three systems benzene+cyclohexane+hexane, acetone+benzene+cyclohexane and acetone+carbon tetrachloride +hexane, although the error can be of 20% in highly non-ideal systems like benzaldehyde diffusing in ethanol+water. ²⁵

Funazukuri et al. determined the limiting diffusion coefficients of vitamin K₃ over the full composition range of CO₂+hexane mixtures at 313.16 K and 16 MPa ¹⁴ and of linoleic acid methyl ester and indole in the same solvent mixtures 313,16 K and 25 MPa. ¹³ In all cases, the Le Blanc equation was better than Wilke-Chang or Perkins-Geankoplis. Simons and Ponters²⁶ studied again the diffusion of carbon dioxide in aqueous ethanol solutions, and compared the results with Holmes-Olander-Wilke, Le Blanc, Lefler-Cullinam and the two equations of Tang-Himmelblau, verifying that only these two equations of Tang-Himmelblau were roughly good. The interactions between the dilute solute and one of the solvent in the mixture have been qualitatively or semiquantitatively analyzed, emphasizing the diffusion decrease because solute+solvent cluster formation through hydrogen bonds. ⁴ In that way, Smith et al. ¹⁹ tried to determine the methanol+benzoic acid and methanol+acridine cluster size in the system CO₂+5.5% alcohol mole fraction with the Wilke-Chang equation, although rejecting the effect of the alcohol in the mixture viscosity. The deviation of $D_{lm}^{\infty}\eta_m$ from linearity with respect to solvent composition has been used to measure such interactions. ^{27 - 30}

2.2. Extension of the Lysis-Ratcliff and Mohan-Srinivasan models. According these authors, the ethanol molecules (*B*) polymerize, and the solute (*A*) forms complexes with the polymers. Both polymerization and complexation are treated like chemical reactions, as



A_1 and B_1 are the molecules of solute and solvent that are free in the dissolution. A mass balance to the ethanol yields

$$\begin{aligned} x_B &= x_{B_1} + 2x_{B_2} + 3x_{B_3} + \dots + nx_{B_n} = x_{B_1} + 2K_{B_2}^{eq}x_{B_1}^2 + 3K_{B_3}^{eq}x_{B_1}x_{B_1} + \dots + nK_{B_n}^{eq}x_{B_1}x_{B_{n-1}} = \\ &= x_{B_1} + 2K_{B_2}^{eq}x_{B_1}^2 + 3K_{B_3}^{eq}K_{B_2}^{eq}x_{B_1}^3 + \dots + nK_{B_n}^{eq}K_{B_{n-1}}^{eq}K_{B_{n-2}}^{eq} \dots K_{B_3}^{eq}K_{B_2}^{eq}x_{B_1}^n \end{aligned} \quad (9)$$

where x_B is the total molar fraction of ethanol in the mixture CO₂+ethanol, and the molar fraction of free ethanol is

$$x_{B_1} = \frac{(2K_B^{eq}x_B + 1) - \sqrt{(2K_B^{eq}x_B + 1)^2 - 4(K_B^{eq}x_B)^2}}{2(K_B^{eq})^2x_B} \quad (10)$$

Carrying out the mass balance for the solute and supposing that the equilibrium constants are also the same

$$x_A = x_{A_1} + x_{A_1B_1} + x_{A_1B_2} + x_{A_1B_3} + \dots + x_{A_1B_n} = x_{A_1} + K_{A_1B_1}^{eq}x_{A_1}x_{B_1} + K_{A_1B_2}^{eq}x_{A_1}x_{B_2} + \dots + K_{A_1B_n}^{eq}x_{A_1}x_{B_{n-1}} \quad (11)$$

$$x_A = x_{A_1} \left[1 + K_{AB}^{eq}(x_{B_1} + x_{B_2} + x_{B_3} + \dots) \right] = x_{A_1} \left[1 + K_{AB}^{eq} \left(\frac{x_{B_1}}{1 - K_B^{eq}x_{B_1}} \right) \right] \quad (12)$$

Bearing in mind eq 12 to differentiate the Fick's law with respect to x_A and including eqs 13 and 14

$$\frac{\partial x_{A_1 B_n}}{\partial x_{A_1}} = K_{AB}^{eq} x_{B_n} \quad (13)$$

$$x_{B_n} = (K_B^{eq})^{n-1} x_{B_1}^n \quad (14)$$

Fick's law becomes

$$D_{AB}^{\infty} \left[1 + K_{AB}^{eq} \left(\frac{x_{B_1}}{1 - K_B^{eq} x_{B_1}} \right) \right] = D_{A_1-m}^{\infty} + K_{AB}^{eq} \left[x_{B_1} D_{A_1 B_1-m}^{\infty} + K_B^{eq} x_{B_1}^2 D_{A_1 B_2-m}^{\infty} + (K_B^{eq})^2 x_{B_1}^3 D_{A_1 B_3-m}^{\infty} + \dots \right] \quad (15)$$

3. Experimental Section

3.1. The Taylor-Aris Technique. This is based on the dispersion of a solute Dirac's delta in a solvent that flows in laminar regime (mean velocity, v_0) through a chromatographic column of length L and internal radius r_0 . After a long residence time (t_R) in the tube, the Dirac's delta becomes a gaussian curve, and the concentration per unit of time at the end of pipe is ³¹

$$C_A(L, t) \propto \sqrt{\frac{1}{2\pi} \left(\frac{v_0^3}{2D_{AB}^{eff} L} \right)} \exp \left[-\frac{(t_R - t)^2}{2 \left(\frac{2D_{AB}^{eff} L}{v_0^3} \right)} \right] \quad (16)$$

where the variance, in units of time, is proportional to an effective binary diffusion coefficient, D_{AB}^{eff}

$$\sigma_t^2 = \left(\frac{2D_{AB}^{eff}L}{v_0^3} \right) = 2D_{AB}^{eff} \frac{t_R^3}{L^2} \quad (17)$$

The molecular diffusion coefficient at infinite dilution of solute, D_{AB}^∞ is calculated with the negative real root of ³²

$$D_{AB}^\infty = \frac{v_0}{4} \left[H \pm \sqrt{H^2 - \left(\frac{r_0^2}{3} \right)} \right] \quad (18)$$

$$H = \frac{2D_{AB}^\infty}{v_0} + \frac{r_0^2 v_0}{24D_{AB}^\infty} \quad (19)$$

H is the plate height. As the variance is related with the width of gaussian peak at the half of total height, $w_{1/2}$,

$$H = \frac{Lw_{1/2}^2}{5.545t_R^2} \quad (20)$$

If the tube is coiled, the effects associated with the coiling will be negligible if ³³⁻³⁷

$$De^2Sc \leq 100 \quad (21)$$

3.2. Chromatograph and the Chemicals. The experimental apparatus consists of a commercial Hewlett-Packard C1205A supercritical fluid chromatograph (HP SFC). This is the same that employed by Gonzalez et al.^{2, 5} in previous studies. It is formed by three parts: the pump module, the oven module and the multiple-wavelength UV detector (MWD). In the pump module there are two reciprocating pumps, one for the supercritical carbon dioxide and the other for the modifier. A mass flow sensor measures the flow rate with an accuracy of $\pm 0.01 \text{ g min}^{-1}$. Also, flow rates were measured at the outlet (at room temperature and atmospheric pressure) with a soap bubble flowmeter. The chromatographic column is located inside the oven module: this is a coiled stainless steel pipe of dimensions 0.762 mm i.d. \times 30.48 m length. The diameter of the coil is 0.26 m. On the oven module is the injection valve, a Rheodyne model 7520 injector of ultralow dispersion with a 0.2 μl loop connected to a port activating the HP SFC software (all the equipment is computer controlled). The variable restrictor is a programmable, backpressure control device located inside the pump module. The HP SFC has two modes of operation: upstream mode and downstream mode. The modes are named for the place in the system where the pressure control occurs. When the apparatus is used in downstream mode, the system pressure is controlled by the variable restrictor, which is located after, or downstream of, the column. In order to reduce the dead volume of the system, low dead volume connections and a low dead volume UV detection cell were utilized.

The four solutes used were supplied by Merck (synthesis grade). Benzyl acetate and 2-phenylethyl acetate have a minimum purity of 99% and 3-phenylpropyl acetate and dibenzyl ether a minimum purity of 98%. The ethanol was also obtained from Merck (LiChrosolv grade, minimum purity of 99.9%) and the carbon dioxide from Air Liquide (minimum purity of 99.998%). The experimental points were obtained at 313.16, 323.16 and 333.16 K and pressures of 15, 20, 25, 30 and 35 MPa over the full concentration range of the mixture (0.0,

2.5, 4.6, 7.1, 10.0, 23.8, 45.4 and 100% mass fraction of ethanol). In these conditions, the system is always monophasic (part of the critical P - T - x_{EtOH} line is available in the literature^{38, 39}). The wavelengths used in the MWD to monitor each solute concentration profile at the end of the column were obtained with a Philips PU 8720 spectrophotometer. Neither carbon dioxide nor ethanol have absorption spectra in the UV zone. One point is the average of 5-10 injections at intervals of 10-15 min for pure CO₂ and 30 min for pure ethanol. The total mass flow varies between 0.14 and 0.12 g/min, and the retention time for all experimental conditions is 100-120 min.

The adsorption of the solute by the inner walls may determine an appreciable asymmetry of the peaks and discrepancies in the elution time of different solvents. Fortunately, no tailing was observed, and the peaks were symmetrical in all the runs. The dispersion curve for all experiments was Gaussian with a linear correlation coefficient of 0.9996-0.9998 between $\ln \langle c \rangle$ and χ^2 ($\langle c \rangle$ being the cross-sectional average concentration and χ being the distance from the peak apex). Peaks that have an asymmetric factor greater than 1.05 have been rejected for analysis.

4. Results and Discussion

The experimental results are shown in Tables 1-4. The reproducibility of the measured diffusivities is normally 3% (absolute average deviation) or better for a total of 5-10 injections. In the table heading, the wavelength at which measurements were made is mentioned. As expected according to hydrodynamic considerations, at constant temperature and pressure, the limiting diffusion coefficient decreases when the mass fraction of ethanol rises. The small maximum that sometimes appears at 2.5% of ethanol and 333.16 K is undoubtedly due to experimental error.

In pure carbon dioxide, benzyl acetate is found to be the fastest diffusing compound, followed by the 2-phenylethylacetate. The diffusion coefficients of 3-phenylpropyl acetate and dibenzyl ether are nearly equal and are lower than those of phenylethylacetate. As can be seen in Table 5 (where data were taken or calculated from the work of Reid et al.²⁴), benzyl acetate is the smallest and lightest substance, and the phenylethylacetate is the second smallest and lightest, which justifies their high diffusivities. Nevertheless, when temperature increases, the difference between 2-phenylethylacetate and the heavier compounds decreases, so the mass and size effect is not constant.

In pure ethanol, benzyl acetate is the fastest substance, and the 3-phenylpropylacetate the slowest, but now, the diffusion coefficients of the phenylpropylacetate and dibenzyl ether are clearly different because the hydrogen bonds between solute and alcohol. The diffusivities of dibenzyl ether and 2-phenylethylacetate are intermediate and similar. At 313.15 K the ester diffuses faster than ether, but at 323.15 K the D_{AB}^{∞} values of the ether are higher than the diffusivities of the ester.

The evolution of diffusivities with ethanol concentration are shown in Figures 1-4. In Figure 1, as D_{AB}^{∞} decreases with the mass fraction of the alcohol, the pressure dependence decreases as well. In Figure 2 the lines that join experimental data are not parallel, but the slope does not greatly vary, which indicates that the temperature dependence is not so affected by the alcohol fraction as the pressure dependence. Figures 3 and 4 are similar: D_{AB}^{∞} decreases monotonically with the mass fraction of ethanol at one fixed pressure or at one fixed temperature.

4.1. Comparison of Diffusivities in Pure CO₂ with Predictive Equations. To predict the diffusion coefficient at infinite dilution in supercritical carbon dioxide, a lot of equations can be employed. They are Lai-Tan,⁴⁰ Hippler-Schubert-Troe,^{41, 42} Woerlee,⁴³ Liu-Ruckenstein cluster,⁴⁴ Liu-Silva-Macedo,⁴⁵ Dariva-Coelho-Oliveira,^{46, 47} Liu-Ruckenstein RHS,⁴⁸ Zhu-Lu-Zhou-Wang-Shi,⁴⁹ Catchpole-King,⁵⁰ Eaton-Akgerman,⁵¹ He of 1997,⁵² He of 1998,⁵³ He-Yu of 1997,⁵⁴ He-Yu of 1998,⁵⁵ Funazukuri-Ishiwata-Wakao,⁵⁷ Funazukuri-Wakao,⁹ and Funazukuri-Kong-Kagei.⁹ Critical properties, acentric factor, and normal boiling temperature are required to calculations and are shown in Table 6. The Average Absolute Deviations (AAD) of these predictive equations are in Table 7.

The densities of supercritical CO₂ were calculated by the Pitzer-Schreiner equation of state,⁶¹ and the viscosities were taken from Stefan and Lucas.⁶²

In Figure 5, the calculated diffusivities of dibenzyl ether in pure carbon dioxide are plotted against experimental ones. For clarity, in the figure, only the results of the equations with lower deviations are represented. The best formulas for the four compounds studied are those of Catchpole-King and He-Yu of 1998, but both overestimates the diffusivities at 15 MPa.

4.2. Comparison of Diffusivities in Pure Ethanol with Predictive Equations. For pure ethanol, the equations of He, He-Yu, Catchpole-King, Eaton-Akgerman, Woerle, Hippler-Schubert-Troe and Sun-Chen can be applied. The Sun-Chen equation^{63, 64} is only valid for solvents such as alkanes and alcohols in the ranges $0.54 \leq T_{rB} \leq 1.07$ and $\rho_{rB} > 1.35$.

$$D_{AB}^{\infty} = \frac{4.17 \times 10^{-16} T}{\eta_B^{0.799} V_{cA}^{0.490}} \quad (22)$$

Only the equations of Woerle, Hippler-Schubert-Troe and Sun-Chen were used in the present work because experimental conditions ($0.61 \leq T_{rB} \leq 0.65$ and $2.79 \leq \rho_{rB} \leq 2.90$) are out of the validity range of the others.⁵⁰⁻⁵⁵ Nevertheless, overestimations are expected because the solute-solvent interactions. So, in eq 22 the following modification is carried out: a solute+solvent cluster formed by one solute molecule and n molecules of ethanol diffuses ($n=2$ for esthers and $n=1$ for ethers). Curiously, Woerlee and Hippler-Schubert-Troe subestimate the diffusivities.

In Figure 6, the overestimation of eq 22 and the underestimation of Woerlee and Hippler-Schubert-Troe can be seen, together with the good results of adding the n molecules of ethanol. The numerical values of AAD for the four substances are presented in Table 8, where it can be seen that the modification made in eq 22, replacing V_{cA} by $V_{cA+nV_{cB}}$ gives the best predictions. Densities and viscosities of pure ethanol were taken from the literature.^{65, 66}

4.3. Comparison of Diffusivities in Mixtures with Predictive Equations. Densities and viscosities of mixtures in the experimental conditions are shown in Tables 9 and 10. Densities were directly obtained or extrapolated from Pöhler and Kiran⁶⁷ and Zúñiga-Moreno and Galicia-Luna.⁶⁸ Nevertheless, the data of Pöhler and Kiran (measured at $1.0 > x_{CO_2} > 0.5$ and $x_{CO_2} = 0.0$) are higher than those of Zúñiga-Moreno and Galicia-Luna for mixtures and higher than the accepted true values for pure solvents,^{61, 65} which indicates the presence of systematic errors in the measurements. When the true values of CO₂ and ethanol are plotted against the data of Pöhler and Kiran, a straight line of slope 0.9742 is obtained, so this

numerical value was employed as a correction factor for all the mixture densities reported by these authors.

There are no viscosities available for the system CO₂+ethanol in the literature. Tilly et al.⁶⁹ report having measured them in supercritical CO₂ +5% mole fraction of ethanol, but neither figures nor tables are provided. Tilly et al. only said that Chung's method²⁴ is the best to estimate viscosities, coinciding with Funazukuri,^{13, 14} who employed the same method for the CO₂+hexane system, and with Souvignet and Olesik¹⁵ for the ternary system ethanol+CO₂+H₂O. In this study, Chung's formulas were used, except for pure solvents, with available viscosities.^{62, 66}

Le Blanc underestimates the diffusivities and the rest of equations overestimate them, especially the Wilke-Chang formula, as can be seen in Figure 7 for dibenzyl ether. The other four equations of Table 11 give results that are not very different, so for clarity, only the Tang-Himmelblau II formula is plotted. It has to be pointed out that between 3×10^{-9} and 5×10^{-9} m² s⁻¹ (mass fraction of 45.4% of ethanol) these four expressions considerably overestimate the diffusivities. This overestimation at high alcohol concentration is common for the four benzene derivatives studied.

4.4. Polymerization and Complexation over the Full Composition Range. The diffusion of the cluster A_1B_n in the mixture m will be the diffusion of one solute which volume and mass are V_A+nV_B and M_A+nM_B , respectively, but one of the eqs 2-8 has to be elected to calculate $D_{A_1B_n-m}^\infty$ in eq 15. Moreover, these formulas (except the Wilke-Chang one) require the limiting binary diffusivities of clusters in pure solvents:

- In pure CO₂, He or He-Yu indicate that⁵²⁻⁵⁵

$$D_{A_1B_n-CO_2}^\infty = \sqrt{\frac{M_A}{M_A + nM_B}} D_{A_1-CO_2}^\infty \quad (23)$$

- In pure ethanol, the diffusivity of the cluster A_1B_n cannot be calculated from experimental data, so the modified Sun-Chen has been employed

$$D_{A_1B_n-B}^\infty = \frac{4.17 \times 10^{-16} T}{\eta_B^{0.799} (V_{cA} + nV_{cB})^{0.490}} \quad (24)$$

The polymerization constant of ethanol is 393.5 at 298.16 K, according to Mohan and Srnivasan.²² The Vant Hoff equation fixes its dependence with temperature as

$$\frac{\partial \ln K_B^{eq}}{\partial (1/T)} = -\frac{\Delta H_B^{hb}}{R} \quad (25)$$

where ΔH_B^{hb} is the hydrogen-bonding enthalpy, that can be aproximated⁷⁰ by -25 kJ/mol. The complexation constants for benzyl acetate, 2-phenylethyl acetate, 3-phenylpropyl acetate and dibenzyl ether are unknown, have to be treated as adjustable parameters, and are shown in Table 12.

With the help of the software FORTRAN POWER STATION 4.0, for values of n higher than 500 no change in the global results is observed, and the Tang-Himmelblau II is observed to be the best equation to calculate $D_{A_1B_n-m}^\infty$

$$\ln(\eta_m^{1/2} D_{A_1 B_n - m}^\infty) = x_{CO_2} \ln(\eta_{CO_2}^{1/2} D_{A_1 B_n - CO_2}^\infty) + x_B \ln(\eta_B^{1/2} D_{A_1 B_n - B}^\infty) \quad (26)$$

The correlation is good, particularly if it is borne in mind that the equilibrium constants are not expressed in fugacities, but molar fractions. The use of fugacities will overly increase the mathematical complexity.

The highest deviations are at 45,4% of alcohol where diffusivities are systematically overestimated, as can be seen in Figure 8 for benzyl acetate. In Figures 9 and 10, it is shown that the overestimation varies with pressure, being more pronounced at low ones. This pressure dependence can indicate that fugacities are necessary for an improvement in the correlation.

5. Conclusions

Limiting binary diffusion coefficients of benzyl acetate, 2-phenylethyl acetate, 3-phenylpropyl acetate, and dibenzyl ether were measured in carbon dioxide, ethanol, and in mixtures of both solvents. Experimental results were compared with the predictions of several equations available in the literature, Catchpole-King and He-Yu of 1998 being the best formulas for calculating diffusivities in pure supercritical carbon dioxide. The Sun-Chen equation results to be the most suitable for determining diffusivities in compressed liquid ethanol (although some modifications have to be done in this last expression in order to consider solute-solvent interactions). In CO₂ + ethanol mixtures, Tang-Himmelblau II performs better than other proposed models.

None of the existing models for predicting limiting binary diffusivities in mixed solvents takes into account the polymerization of solute molecules nor solute-solvent interactions. To account for this, Tang-Himmelblau II is extended to regard both cases as chemical reactions. The resulting correlative equation gives good fitting except at intermediate compositions.

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Symbols

C_A = concentration per unit of time in the Taylor-Aris tube, $\text{mol m}^{-3}\text{s}^{-1}$

D = binary diffusion, m^2/s

De = Dean number

f = association factor in the equation of Wilke-Chang

H = plate height of the chromatographic column, m

$K_{B_n}^{eq}$ = polymerization constant

$K_{A_1B_n}^{eq}$ = complexation constant

L = length of the Taylor-Aris tube, m

M = molecular mass, kg mol^{-1}

N = number

P = pressure, Pa

Q^{vdw} = van der Waals parameter of area

R^{vdW} = van der Waals parameter of volume

r_0 = internal radius of the Taylor-Aris tube, m

Sc = Schmidt number

T = absolute temperature, K

T = time, s

t_R = residence time in the Taylor-Aris tube, s

x_i = molar fraction of the i component

V = molar volume, $\text{m}^3 \text{mol}^{-1}$

v_0 = mean velocity in the Taylor-Aris tube, m s^{-1}

$w_{1/2}$ = width of a Gaussian peak at the half of the total height, s

Greek symbols

ΔH_B^{hb} = hydrogen-bonding enthalpy, J mol^{-1}

η = viscosity, $\text{kg m}^{-1} \text{s}^{-1}$

σ_t^2 = variance of the Gaussian curve, s

ω = acentric factor

Superscripts

0 = gas at low pressure

∞ = infinite dilution

eff = effective

Subscripts

1,2,3 = substances of the mixture

1*m* = substance 1 in the mixture

A = solute

*A*₁*B*_{*n*} = complex formed by one molecule of *A* and *n* of *B*

*A*₁*B*_{*n*} - *m* = solute-solvent complex diffusing in the mixture

B = solvent

*B*_{*n*} = polymer formed by *n* molecules of *B*

B = normal boiling point

c = critical conditions

m = mixture

r = reduced conditions

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LIST OF THE CAPTIONS

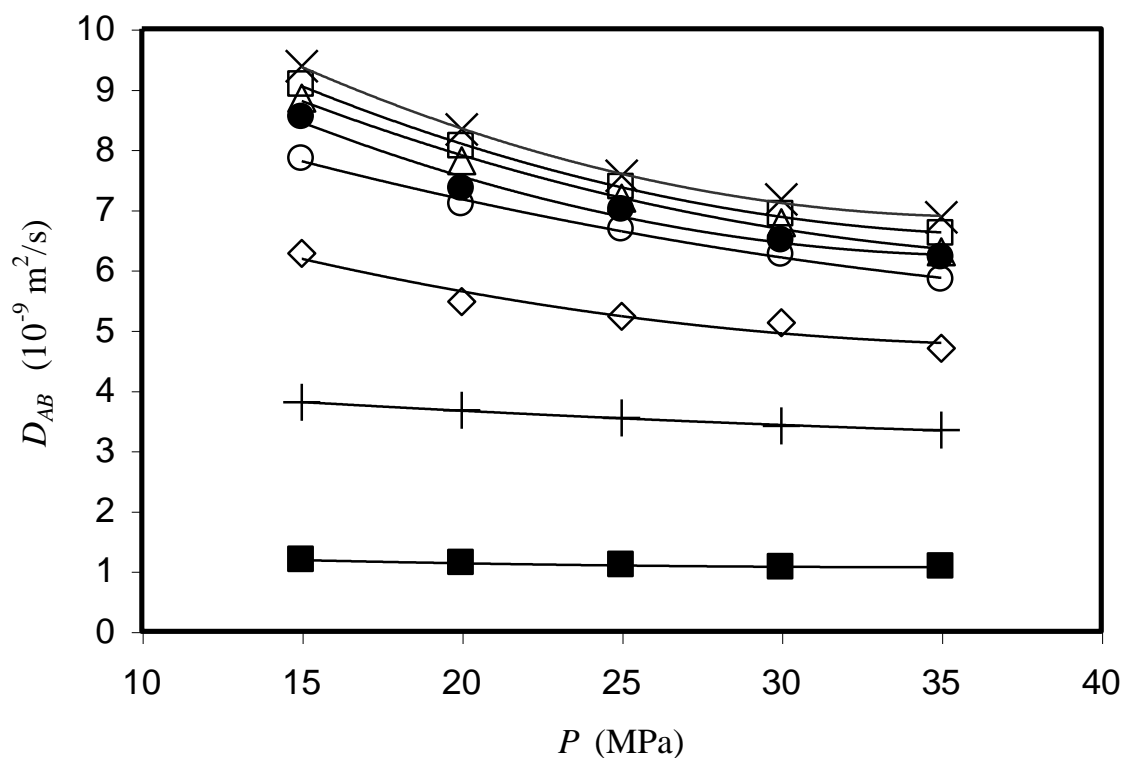


Figure 1. Diffusion coefficients of 3-phenylpropyl acetate in the mixtures of carbon dioxide and ethanol at 323.15 K as a function of pressure: (x) pure CO₂; (□) 2.5% of ethanol; (△) 4.6% of ethanol; (●) 7.1% of ethanol; (○) 10% of ethanol; (◇) 23.8% of ethanol; (+) 45.4% of ethanol; (■) pure ethanol. The lines represent the fitting to equation $D_{AB} = a + b/P$.

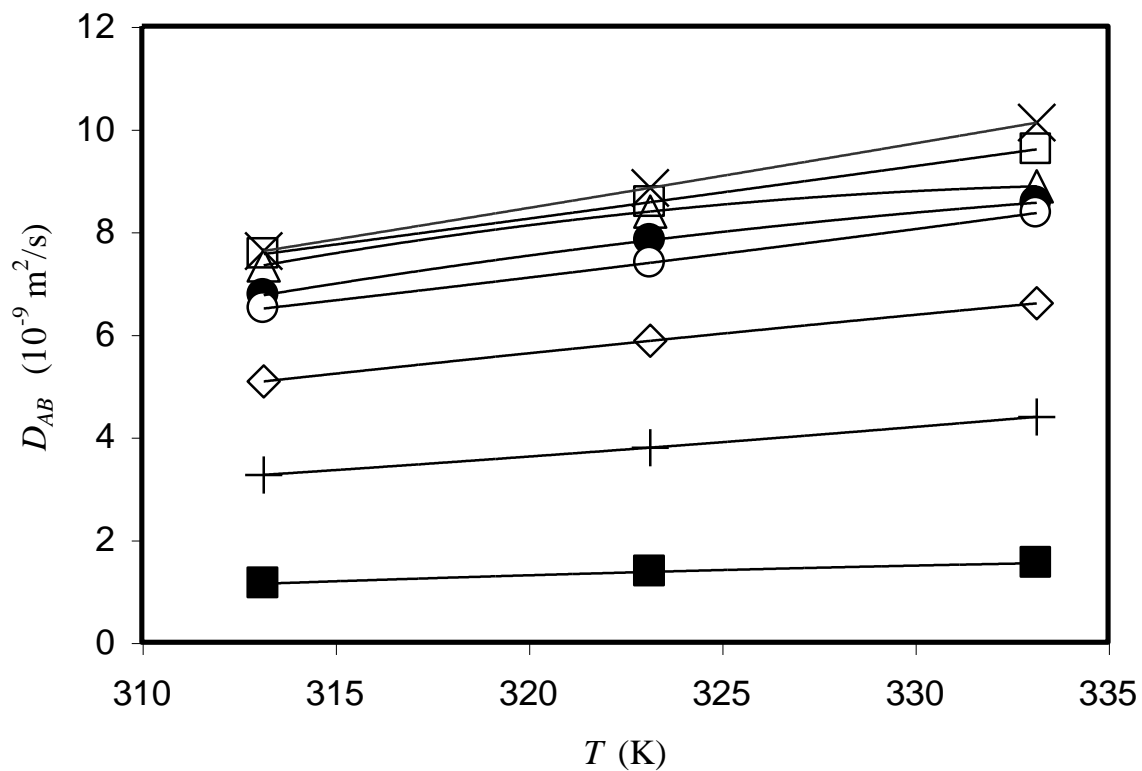


Figure 2. Diffusion coefficients of benzyl acetate in the mixtures of carbon dioxide and ethanol at 25 MPa as a function of temperature. Symbols indicate the same concentrations as in Figure 1. The lines represent the fitting to equation $D_{AB} = c + dT$.

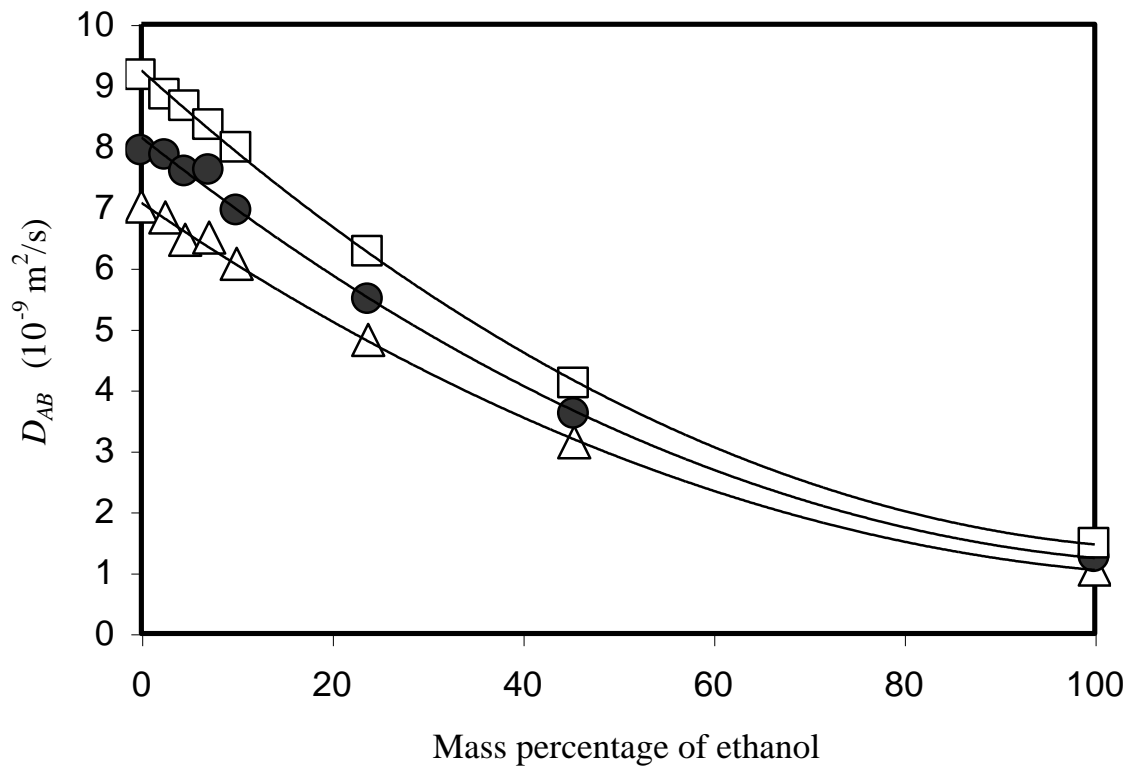


Figure 3. Diffusion coefficients of 2-phenylethyl acetate in the mixtures of carbon dioxide and ethanol at 25 MPa as a function of alcohol percentage: (Δ) 313.15 K; (\bullet) 323.15 K; (\square) 333.15 K. Solid lines are guides for the eye only.

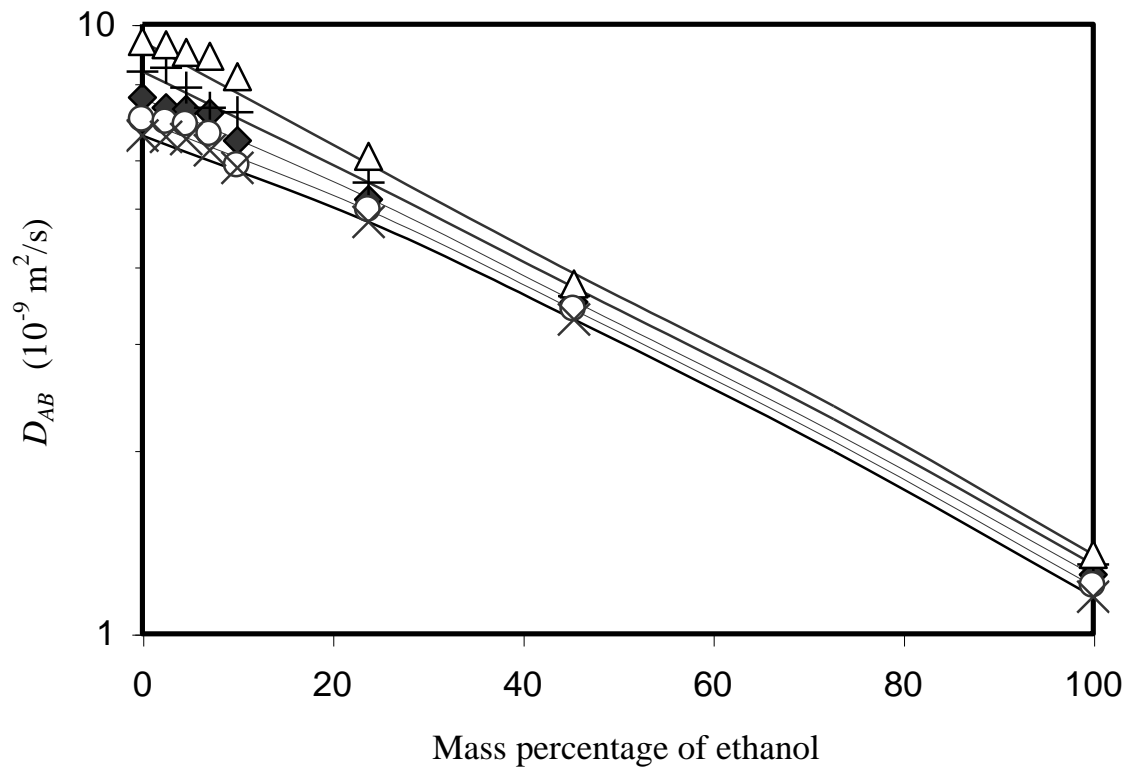


Figure 4. Diffusion coefficients of dibenzyl ether in the mixtures of carbon dioxide and ethanol at 323.15 K as a function of alcohol percentage: (Δ) 15 MPa; (+) 20 MPa; (\blacklozenge) 25 MPa; (O) 30 MPa; (\times) 35 MPa. Solid lines are guides for the eye only.

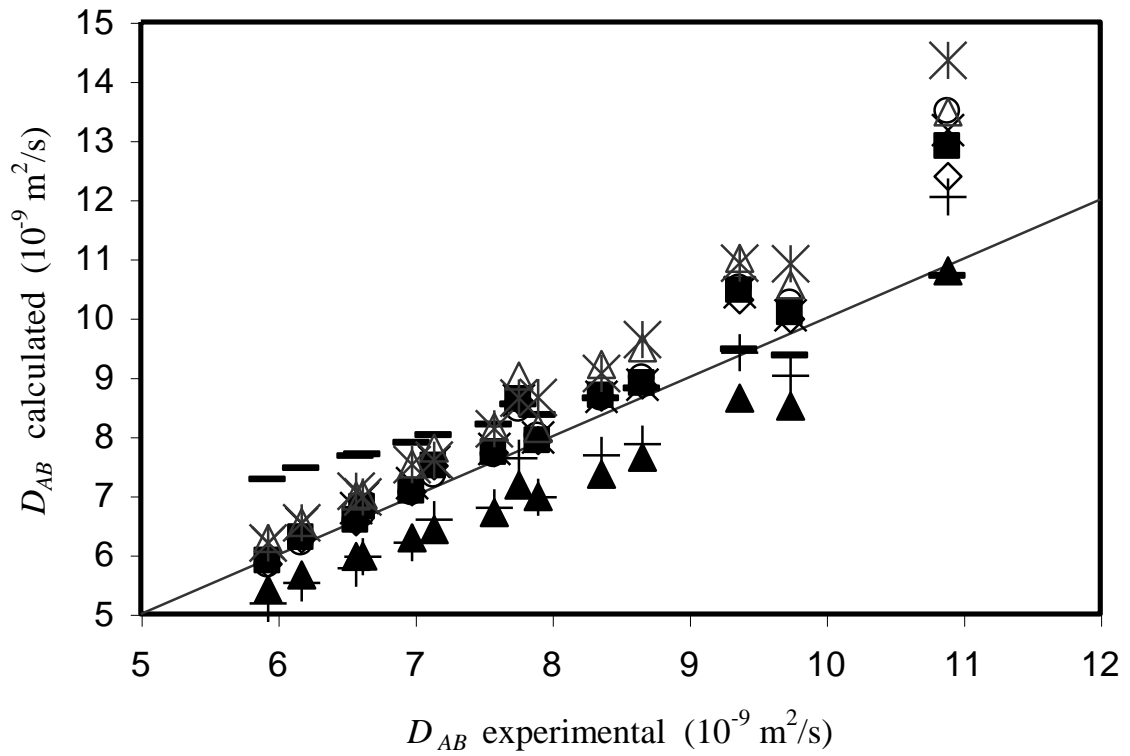


Figure 5. Comparison of experimental and calculated diffusivities of dibenzyl ether in pure carbon dioxide: (○) Catchpole-King; (–) Eaton-Akgerman; (×) He of 1997; (⋈) He of 1998; (△) Funazukuri-Kong-Kagei; (■) He-Yu of 1997, (◇) He-Yu of 1998; (▲) Liu-Silva-Macedo; (+) Dariva-Coelho-Oliveira.

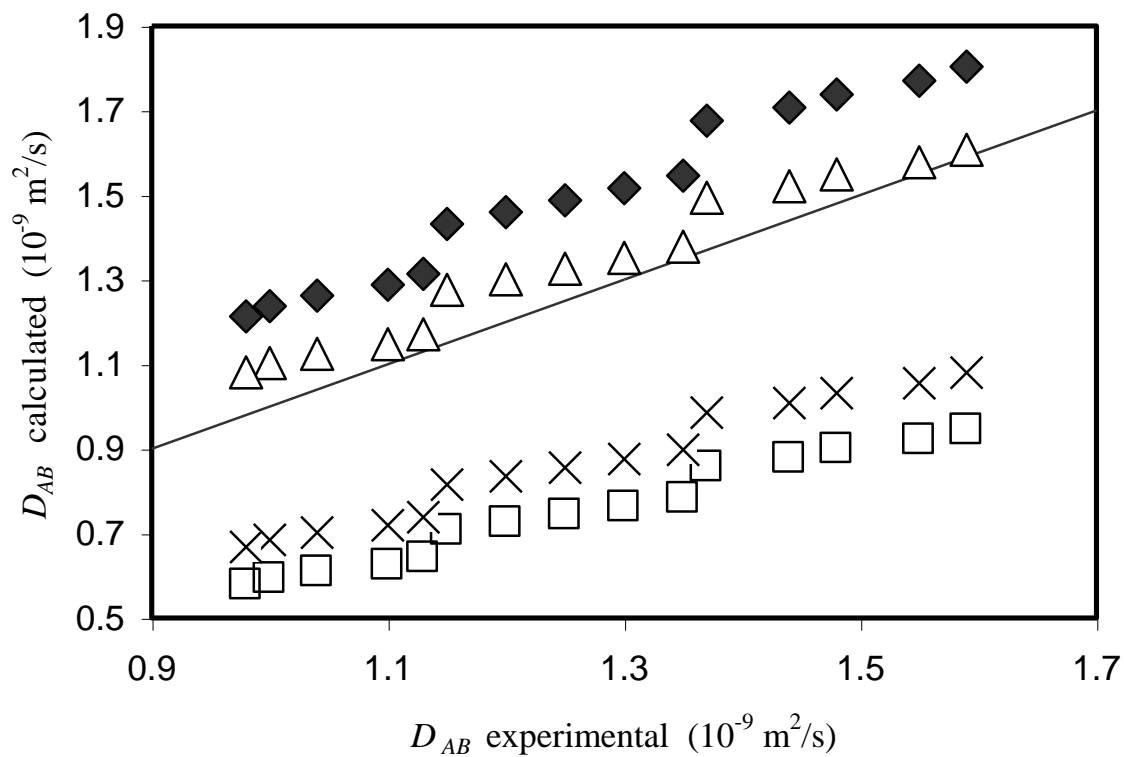


Figure 6. Comparison of experimental and calculated diffusivities of dibenzyl ether in pure ethanol: (x) Hippler-Schubert-Troe; (□) Woerlee; (♦) Sun-Chen; (△) modified Sun-Chen.

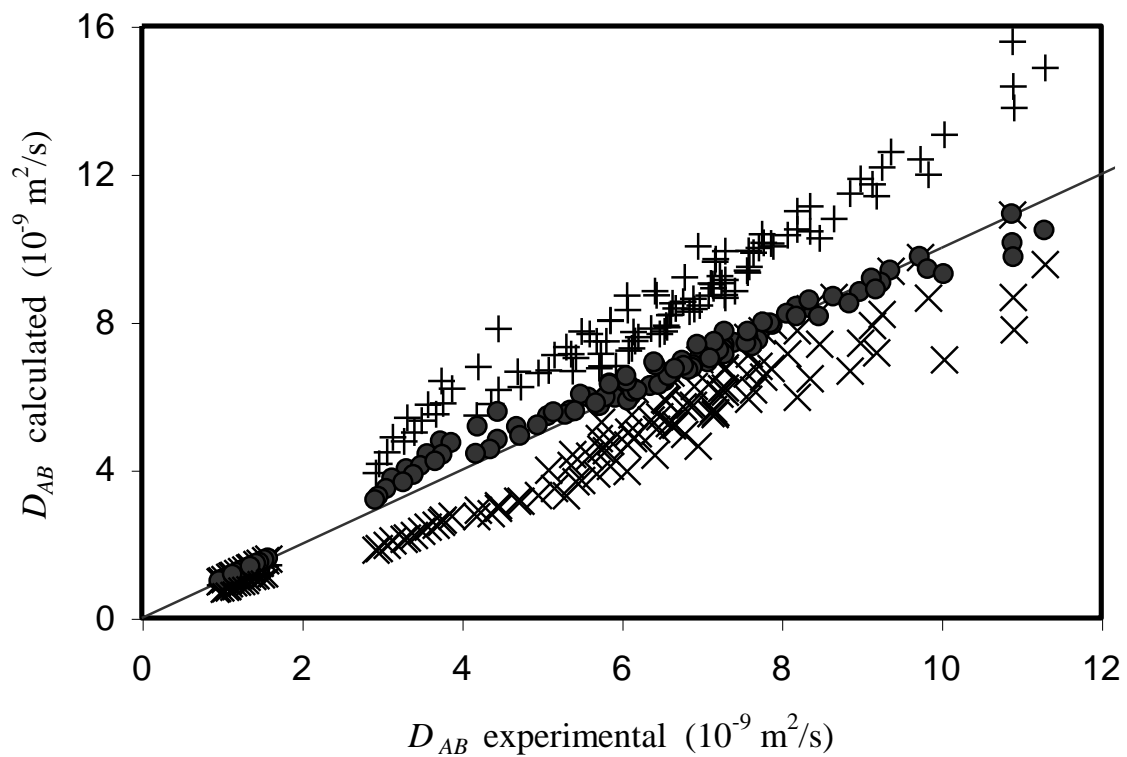


Figure 7. Comparison of experimental and calculated diffusivities of dibenzyl ether in mixtures of carbon dioxide and ethanol: (×) Le Blanc; (+) Wilke-Chang; (●) Tang-Himmelblau II.

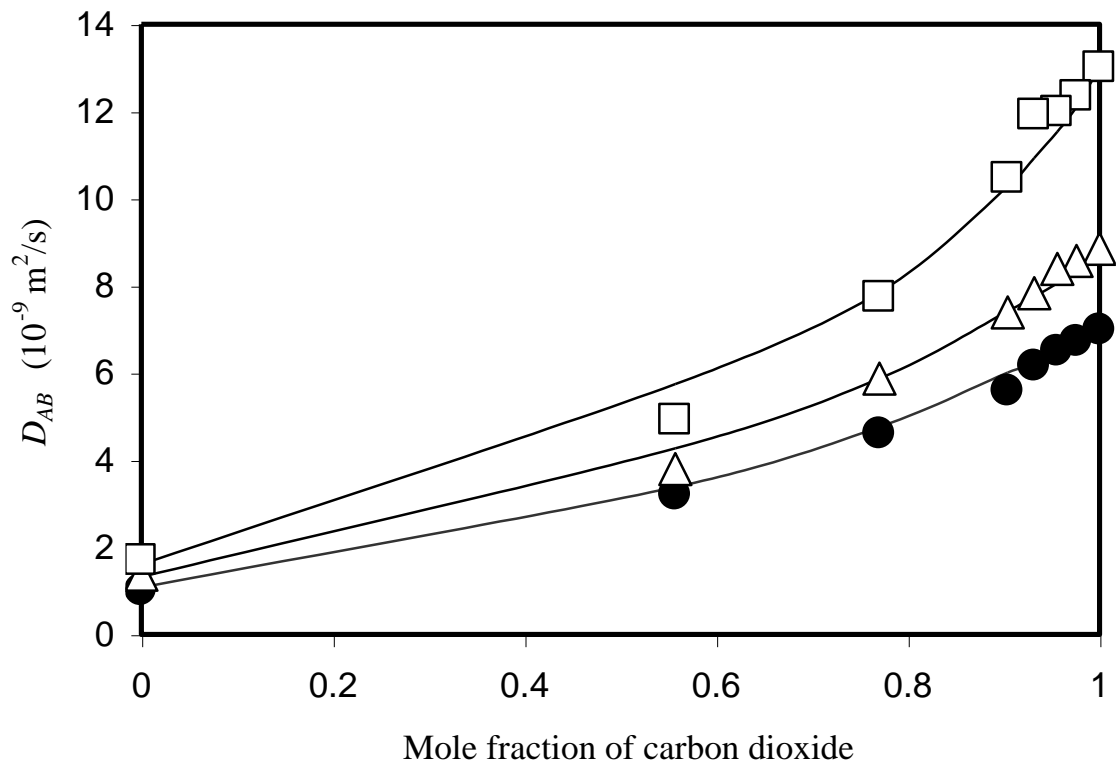


Figure 8. Experimental and calculated diffusion coefficients of benzyl acetate as a function of CO₂ mole fraction: (△) 323.15 K and 25 MPa; (●) 313.15 K and 35 MPa; (□) 333.15 K and 15 MPa. Solid lines correspond to the results of eq 15.

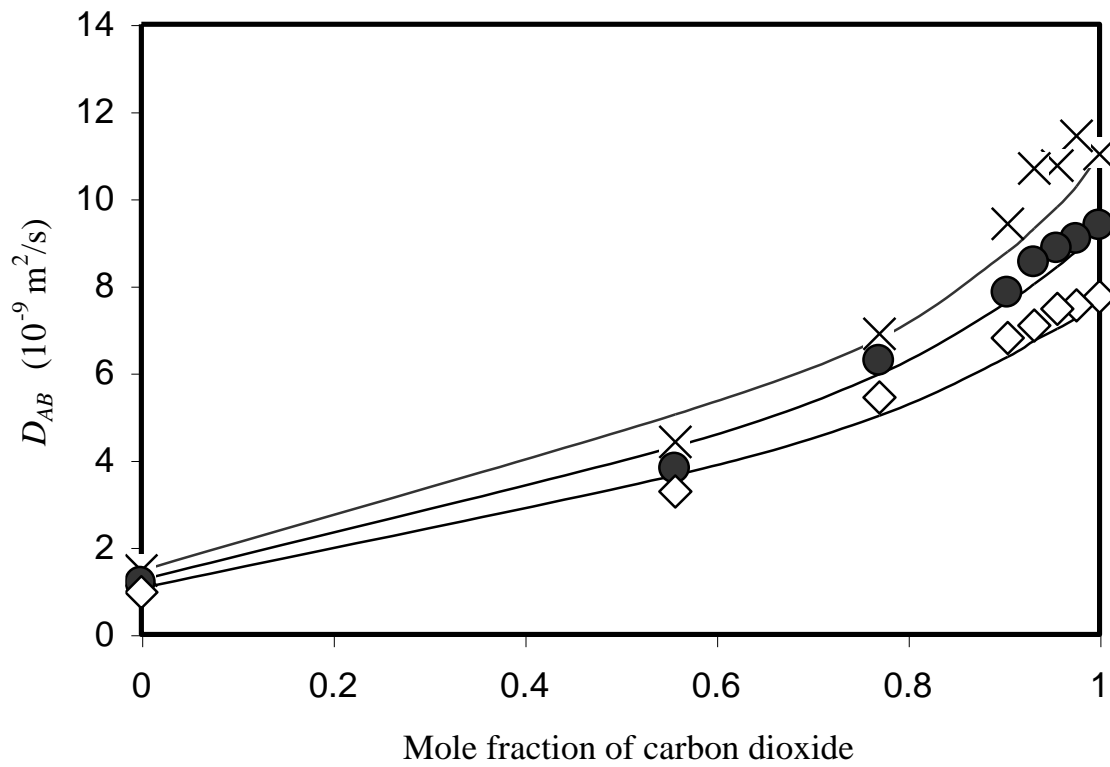


Figure 9. Experimental and calculated diffusion coefficients of 3-phenylpropyl acetate at 15 MPa as a function of CO₂ mole fraction: (x) 333.15 K; (●) 323.15 K; (◇) 313.15 K. Solid lines correspond to the results of eq 15.

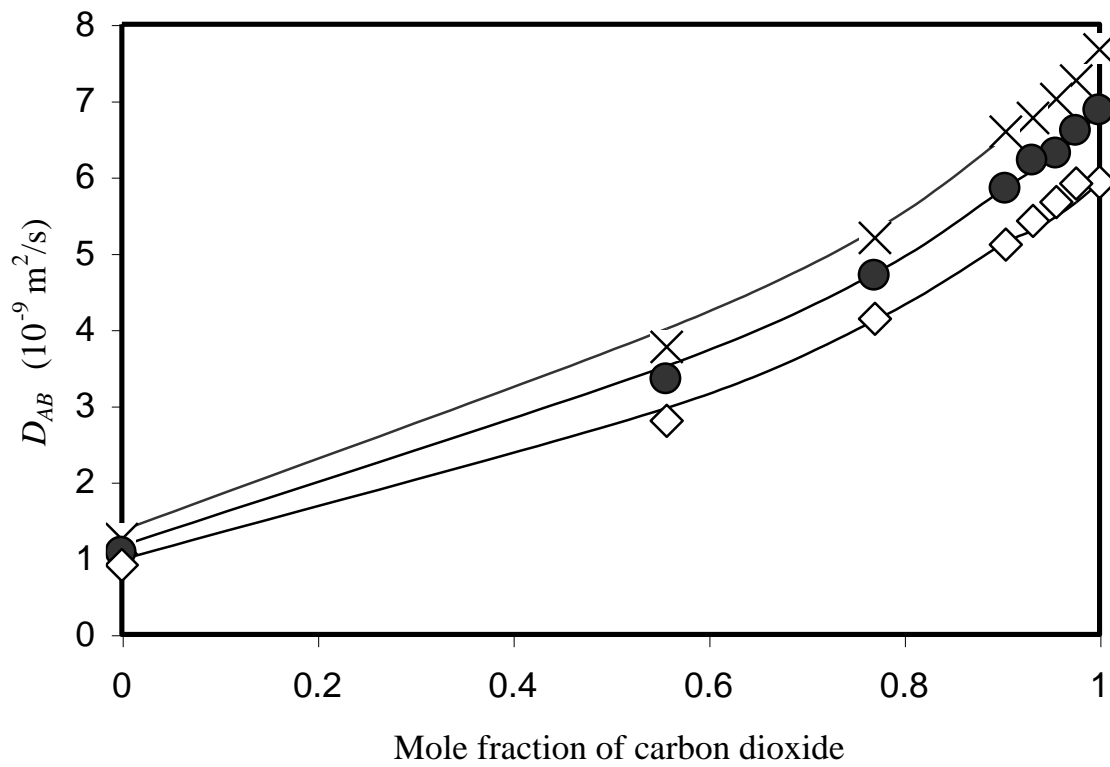


Figure 10. Experimental and calculated diffusion coefficients of 3-phenylpropyl acetate at 35 MPa as a function of CO₂ mole fraction. Symbols are the same that in Figure 10. Solid lines correspond to the results of eq 15.

LIST OF THE TABLES

Table 1. Diffusivities of Benzyl acetate ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) Measured at a Wavelength of 252 nm

conditions		mass percentage of ethanol							
T (K)	P (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	9.30 ± 0.20	9.21 ± 0.13	8.25 ± 0.10	8.18 ± 0.07	7.72 ± 0.05	6.25 ± 0.22	3.58 ± 0.02	1.26 ± 0.02
	20.00	8.21 ± 0.19	8.19 ± 0.11	7.54 ± 0.15	7.21 ± 0.10	6.89 ± 0.06	5.37 ± 0.05	3.34 ± 0.04	1.18 ± 0.01
	25.00	7.62 ± 0.14	7.56 ± 0.13	7.34 ± 0.09	6.76 ± 0.12	6.50 ± 0.13	5.08 ± 0.06	3.26 ± 0.02	1.14 ± 0.01
	30.00	7.39 ± 0.08	7.21 ± 0.04	6.90 ± 0.04	6.49 ± 0.05	6.01 ± 0.09	4.93 ± 0.12	3.12 ± 0.02	1.12 ± 0.01
	35.00	6.99 ± 0.06	6.73 ± 0.06	6.50 ± 0.05	6.16 ± 0.10	5.59 ± 0.08	4.61 ± 0.08	3.21 ± 0.03	1.01 ± 0.01
323.16	15.00	11.37 ± 0.20	10.85 ± 0.21	9.94 ± 0.22	9.59 ± 0.03	9.15 ± 0.04	6.94 ± 0.15	4.28 ± 0.02	1.47 ± 0.01
	20.00	9.94 ± 0.21	9.52 ± 0.25	8.58 ± 0.11	8.08 ± 0.22	8.09 ± 0.04	6.24 ± 0.08	4.01 ± 0.03	1.40 ± 0.02
	25.00	8.85 ± 0.08	8.57 ± 0.08	8.39 ± 0.06	7.83 ± 0.08	7.39 ± 0.23	5.87 ± 0.07	3.79 ± 0.02	1.37 ± 0.02
	30.00	8.22 ± 0.14	8.10 ± 0.08	7.90 ± 0.08	7.19 ± 0.06	6.79 ± 0.21	5.62 ± 0.09	3.66 ± 0.31	1.32 ± 0.02
	35.00	7.56 ± 0.14	7.51 ± 0.27	7.30 ± 0.11	6.71 ± 0.07	6.19 ± 0.18	5.33 ± 0.04	3.59 ± 0.03	1.24 ± 0.01
333.16	15.00	13.01 ± 0.43	12.35 ± 0.27	11.99 ± 0.20	11.92 ± 0.21	10.47 ± 0.17	7.74 ± 0.38	4.92 ± 0.04	1.70 ± 0.05
	20.00	11.79 ± 0.27	10.88 ± 0.23	10.17 ± 0.17	9.54 ± 0.21	9.26 ± 0.09	7.05 ± 0.20	4.66 ± 0.02	1.57 ± 0.02
	25.00	10.12 ± 0.09	9.60 ± 0.05	8.88 ± 0.16	8.56 ± 0.02	8.36 ± 0.17	6.60 ± 0.04	4.39 ± 0.04	1.54 ± 0.02
	30.00	9.18 ± 0.23	8.77 ± 0.10	8.72 ± 0.20	7.94 ± 0.16	7.79 ± 0.14	6.29 ± 0.08	4.22 ± 0.05	1.50 ± 0.01
	35.00	8.41 ± 0.14	8.34 ± 0.06	8.23 ± 0.20	7.47 ± 0.09	7.47 ± 0.11	5.95 ± 0.07	3.93 ± 0.05	1.50 ± 0.01

Table 2. Diffusivities of 2-Phenylethyl Acetate ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) Measured at a Wavelength of 258 nm

conditions		mass percentage of ethanol							
T (K)	P (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	8.27 ± 0.31	8.25 ± 0.11	8.23 ± 0.09	7.58 ± 0.16	7.06 ± 0.11	5.43 ± 0.23	3.41 ± 0.06	1.16 ± 0.01
	20.00	7.49 ± 0.05	7.44 ± 0.13	7.10 ± 0.12	6.94 ± 0.11	6.40 ± 0.06	5.14 ± 0.05	3.22 ± 0.04	1.11 ± 0.02
	25.00	7.01 ± 0.05	6.83 ± 0.09	6.46 ± 0.11	6.50 ± 0.10	6.07 ± 0.10	4.82 ± 0.05	3.14 ± 0.05	1.05 ± 0.01
	30.00	6.72 ± 0.21	6.39 ± 0.05	6.22 ± 0.04	5.97 ± 0.05	5.61 ± 0.06	4.56 ± 0.06	3.01 ± 0.03	1.02 ± 0.01
	35.00	6.07 ± 0.07	6.02 ± 0.17	5.83 ± 0.05	5.65 ± 0.04	5.47 ± 0.05	4.32 ± 0.06	2.96 ± 0.04	0.98 ± 0.01
323.16	15.00	9.94 ± 0.15	9.74 ± 0.26	9.64 ± 0.14	9.28 ± 0.11	8.64 ± 0.18	6.33 ± 0.35	3.99 ± 0.06	1.34 ± 0.01
	20.00	8.75 ± 0.14	8.73 ± 0.14	8.43 ± 0.11	7.87 ± 0.11	7.55 ± 0.15	5.82 ± 0.14	3.70 ± 0.05	1.29 ± 0.02
	25.00	7.92 ± 0.09	7.85 ± 0.08	7.58 ± 0.08	7.60 ± 0.07	6.94 ± 0.11	5.48 ± 0.08	3.60 ± 0.03	1.25 ± 0.02
	30.00	7.46 ± 0.08	7.34 ± 0.07	7.01 ± 0.05	6.78 ± 0.07	6.21 ± 0.13	5.20 ± 0.05	3.44 ± 0.06	1.22 ± 0.01
	35.00	7.06 ± 0.07	7.04 ± 0.20	6.57 ± 0.04	6.28 ± 0.05	5.97 ± 0.09	4.88 ± 0.04	3.43 ± 0.05	1.18 ± 0.02
333.16	15.00	11.43 ± 0.31	11.53 ± 0.09	10.96 ± 0.29	10.75 ± 0.07	10.22 ± 0.07	7.45 ± 0.10	4.53 ± 0.03	1.56 ± 0.02
	20.00	10.16 ± 0.45	9.82 ± 0.20	9.59 ± 0.13	9.28 ± 0.11	9.15 ± 0.20	6.71 ± 0.12	4.28 ± 0.02	1.54 ± 0.08
	25.00	9.16 ± 0.10	8.84 ± 0.11	8.65 ± 0.12	8.34 ± 0.09	7.97 ± 0.17	6.26 ± 0.06	4.10 ± 0.05	1.47 ± 0.02
	30.00	8.33 ± 0.32	8.15 ± 0.05	8.08 ± 0.19	7.81 ± 0.10	7.43 ± 0.10	5.79 ± 0.20	3.99 ± 0.07	1.40 ± 0.01
	35.00	7.90 ± 0.09	7.74 ± 0.05	7.62 ± 0.08	7.26 ± 0.07	6.96 ± 0.08	5.62 ± 0.07	3.79 ± 0.03	1.37 ± 0.01

Table 3. Diffusivities of 3-Phenylpropyl Acetate ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) Measured at a Wavelength of 267 nm

conditions		mass percentage of ethanol							
<i>T</i> (K)	<i>P</i> (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	7.75 ± 0.07	7.55 ± 0.09	7.47 ± 0.15	7.09 ± 0.17	6.80 ± 0.10	5.44 ± 0.14	3.28 ± 0.06	0.97 ± 0.08
	20.00	7.14 ± 0.13	7.07 ± 0.15	6.76 ± 0.07	6.53 ± 0.05	6.21 ± 0.08	4.84 ± 0.07	3.16 ± 0.01	0.98 ± 0.01
	25.00	6.61 ± 0.12	6.44 ± 0.12	6.33 ± 0.12	6.03 ± 0.09	5.92 ± 0.08	4.56 ± 0.08	3.01 ± 0.03	0.94 ± 0.00
	30.00	6.34 ± 0.12	6.14 ± 0.07	5.97 ± 0.06	5.75 ± 0.07	5.42 ± 0.11	4.29 ± 0.08	2.91 ± 0.02	0.93 ± 0.00
	35.00	6.06 ± 0.29	5.91 ± 0.03	5.67 ± 0.02	5.42 ± 0.05	5.11 ± 0.08	4.14 ± 0.14	2.80 ± 0.13	0.91 ± 0.01
323.16	15.00	9.38 ± 0.31	9.07 ± 0.11	8.85 ± 0.17	8.53 ± 0.05	7.84 ± 0.16	6.27 ± 0.18	3.80 ± 0.03	1.18 ± 0.01
	20.00	8.33 ± 0.27	8.05 ± 0.24	7.81 ± 0.15	7.35 ± 0.10	7.09 ± 0.10	5.47 ± 0.09	3.67 ± 0.06	1.13 ± 0.02
	25.00	7.56 ± 0.13	7.37 ± 0.09	7.19 ± 0.16	7.00 ± 0.15	6.67 ± 0.07	5.23 ± 0.07	3.54 ± 0.06	1.10 ± 0.01
	30.00	7.17 ± 0.05	6.92 ± 0.12	6.78 ± 0.12	6.49 ± 0.09	6.25 ± 0.08	5.12 ± 0.07	3.41 ± 0.05	1.06 ± 0.00
	35.00	6.87 ± 0.20	6.60 ± 0.17	6.30 ± 0.08	6.21 ± 0.09	5.84 ± 0.59	4.70 ± 0.07	3.34 ± 0.06	1.07 ± 0.01
333.16	15.00	11.02 ± 0.32	11.44 ± 0.32	10.76 ± 0.19	10.69 ± 0.42	9.42 ± 0.20	6.90 ± 0.34	4.42 ± 0.06	1.47 ± 0.03
	20.00	10.05 ± 0.53	9.48 ± 0.12	8.86 ± 0.11	8.43 ± 0.15	8.19 ± 0.09	6.26 ± 0.16	4.17 ± 0.06	1.37 ± 0.02
	25.00	8.63 ± 0.12	8.30 ± 0.04	8.20 ± 0.11	7.68 ± 0.14	7.43 ± 0.12	5.84 ± 0.08	3.93 ± 0.03	1.36 ± 0.03
	30.00	8.11 ± 0.30	7.59 ± 0.06	7.60 ± 0.52	7.20 ± 0.09	7.09 ± 0.23	5.60 ± 0.06	3.86 ± 0.06	1.26 ± 0.02
	35.00	7.67 ± 0.14	7.26 ± 0.07	7.02 ± 0.10	6.77 ± 0.08	6.59 ± 0.14	5.20 ± 0.08	3.77 ± 0.03	1.25 ± 0.01

Table 4. Diffusivities Dibenzyl Ether ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) Measured at a Wavelength of 257 nm

conditions		mass percentage of ethanol							
T (K)	P (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	7.76 ± 0.09	7.72 ± 0.07	7.65 ± 0.11	7.18 ± 0.19	6.79 ± 0.06	5.31 ± 0.15	3.32 ± 0.03	1.13 ± 0.04
	20.00	7.14 ± 0.06	7.09 ± 0.12	6.90 ± 0.11	6.64 ± 0.05	6.08 ± 0.07	4.70 ± 0.08	3.14 ± 0.05	1.10 ± 0.01
	25.00	6.62 ± 0.04	6.56 ± 0.07	6.37 ± 0.10	6.15 ± 0.30	5.60 ± 0.06	4.46 ± 0.03	3.07 ± 0.02	1.04 ± 0.01
	30.00	6.17 ± 0.06	6.13 ± 0.05	6.09 ± 0.10	5.74 ± 0.09	5.37 ± 0.06	4.37 ± 0.08	2.97 ± 0.03	1.00 ± 0.01
	35.00	5.93 ± 0.03	5.75 ± 0.17	5.72 ± 0.10	5.39 ± 0.09	5.09 ± 0.05	4.19 ± 0.08	2.93 ± 0.03	0.98 ± 0.01
323.16	15.00	9.37 ± 0.21	9.26 ± 0.23	8.99 ± 0.20	8.86 ± 0.10	8.20 ± 0.16	6.07 ± 0.12	3.75 ± 0.03	1.35 ± 0.03
	20.00	8.36 ± 0.03	8.48 ± 0.25	7.87 ± 0.18	7.30 ± 0.12	7.17 ± 0.08	5.50 ± 0.09	3.58 ± 0.03	1.30 ± 0.01
	25.00	7.58 ± 0.04	7.30 ± 0.09	7.25 ± 0.10	7.15 ± 0.05	6.44 ± 0.06	5.16 ± 0.06	3.50 ± 0.02	1.25 ± 0.01
	30.00	6.98 ± 0.07	6.91 ± 0.05	6.85 ± 0.03	6.60 ± 0.04	5.86 ± 0.19	4.96 ± 0.09	3.41 ± 0.08	1.20 ± 0.01
	35.00	6.57 ± 0.08	6.54 ± 0.18	6.48 ± 6.41	6.21 ± 0.10	5.81 ± 0.17	4.74 ± 0.10	3.28 ± 0.03	1.15 ± 0.01
333.16	15.00	10.89 ± 0.63	11.30 ± 0.21	10.90 ± 0.19	10.91 ± 0.14	10.04 ± 0.08	6.96 ± 0.34	4.46 ± 0.03	1.59 ± 0.01
	20.00	9.74 ± 0.14	9.84 ± 0.12	9.14 ± 0.11	9.19 ± 0.05	8.36 ± 0.80	6.42 ± 0.10	4.21 ± 0.06	1.55 ± 0.06
	25.00	8.66 ± 0.15	8.20 ± 0.16	8.08 ± 0.20	7.78 ± 0.11	7.59 ± 0.12	5.86 ± 0.07	3.88 ± 0.05	1.48 ± 0.01
	30.00	7.90 ± 0.08	7.60 ± 0.20	7.57 ± 0.16	7.23 ± 0.14	7.12 ± 0.16	5.69 ± 0.03	3.77 ± 0.03	1.44 ± 0.01
	35.00	7.42 ± 0.06	7.29 ± 0.12	7.30 ± 0.13	6.77 ± 0.07	6.68 ± 0.09	5.43 ± 0.11	3.68 ± 0.04	1.37 ± 0.01

Table 5. Molar Mass and van der Waals Parameters of the Studied Substances

substance	formula	M	R^{vdW}	Q^{vdW}
		($10^{-3}\text{kg mol}^{-1}$)		
benzyl acetate	$\text{C}_9\text{H}_{10}\text{O}_2$	150.80	5.5992	4.388
2-phenylethyl acetate	$\text{C}_{10}\text{H}_{12}\text{O}_2$	164.10	6.2736	4.928
3-phenylpropyl acetate	$\text{C}_{11}\text{H}_{14}\text{O}_2$	178.30	6.9480	5.468
dibenzyl ether	$\text{C}_{14}\text{H}_{14}\text{O}$	198.26	7.6361	5.560

Table 6. Properties of Employed Substances

substance	$10^5 P_c$		V_c	ω	
	T_c (K)	T_b (K)	($10^{-6} \text{m}^3 \text{mol}^{-1}$)		
benzyl acetate ^a	699.01	486.66	31.80	449.00	0.4699
2-phenyl ethyl acetate ^b	712.23	505.16	30.12	524.15	0.5442
3-phenylpropyl acetate ^b	718.70	518.16	27.23	580.37	0.5924
dibenzyl ether ^a	777.01	561.46	25.60	634.00	0.5907
carbon dioxide ^c	304.14	216.55	73.75	94.00	0.23900
ethanol ^c	514.00	351.44	61.37	168.00	0.64400

^a From HYSYS database. ^b Normal boiling temperatures from Lide⁵⁸ and Merck catalog.⁵⁹ Critical properties calculated as the average of group contribution methods of Joback²⁴ and Wen-Qiang.⁶⁰ The acentric factor was obtained from the formula of Lee-Kesler.²⁴ ^c From ref 71.

Table 7. AAD (%) of Several Predictive Equations in Pure Carbon Dioxide

equation	benzyl acetate	2-phenylethyl acetate	3-phenylpropyl acetate	dibenzyl ether
Lai-Tan	28.09	36.36	38.27	36.52
Liu-Ruckenstein cluster	13.09	18.17	17.93	15.05
Woerlee	19.46	19.28	21.35	25.58
Hippler-Schubert-Troe	16.28	22.66	23.56	21.09
Catchpole-King	3.45	7.17	7.18	4.46
Eaton-Akgerman	4.99	7.45	9.92	9.63
He of 1997	3.49	9.88	10.09	5.66
He of 1998	7.75	14.72	14.91	10.31
He-Yu of 1997	2.94	8.29	8.5	4.42
He-Yu of 1998	2.66	7.62	7.83	3.92
Funazukuri-Hachisu-Wakao	15.59	20.9	19.36	13.94
Funazukuri-Ishiwata-Wakao	33.33	40.94	40.22	37.11
Funazukuri-Wakao	64.77	77.04	79.07	75.89
Funazukuri-Kong-Kagei	8.94	14.54	13.54	9.59
Liu-Ruckenstein RHS	18.91	22.75	22.06	17.54
Liu-Silva-Macedo	9.98	4.47	4.59	9.5
Zhu-Lu-Zhou-Wang-Shi	14.6	18.5	18.47	14.36
Dariva-Coelho-Oliveira	7.82	6.45	7.36	9.13

Table 8. AAD (%) of Four Predictive Equations in Pure Ethanol

substance	Sun-Chen	modified Sun-Chen	Woerlee	Hippler- Schubert- Troie
benzyl acetate	31.06	2.79	30.31	28.64
2-phenylethyl acetate	30.31	2.84	32.58	27.31
3-phenylpropyl acetate	38.45	10.69	29.66	21.54
dibenzyl ether	18.97	6.03	40.50	31.65

Table 9. Densities of CO₂+Ethanol Mixtures (kg m⁻³)

conditions		mass percentage of ethanol							
<i>T</i> (K)	<i>P</i> (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	781.00	780.73	780.62	781.10	793.12	830.08	836.56	780.39
	20.00	840.80	836.82	834.25	831.72	830.61	860.28	862.40	784.45
	25.00	880.70	874.98	871.14	867.05	860.01	883.76	883.78	788.34
	30.00	911.20	905.29	900.70	895.68	885.48	903.01	901.10	792.07
	35.00	936.10	930.28	925.19	919.55	907.49	919.35	915.16	795.67
323.16	15.00	700.80	708.04	715.51	725.11	736.37	785.81	804.79	772.36
	20.00	784.90	782.90	783.16	785.01	788.47	824.32	832.33	776.64
	25.00	835.00	830.56	827.93	826.19	825.67	851.95	852.32	780.73
	30.00	871.40	865.91	862.08	858.47	855.92	873.74	867.71	784.65
	35.00	900.00	894.85	890.67	886.07	881.15	891.82	879.90	788.41
333.16	15.00	607.10	626.63	640.95	657.03	676.64	749.06	762.87	764.19
	20.00	724.60	727.93	733.54	739.95	743.83	793.11	801.37	768.71
	25.00	781.20	785.28	786.45	787.98	789.09	823.73	825.54	773.02
	30.00	830.50	827.17	825.70	824.37	824.33	847.43	842.71	777.13
	35.00	864.00	860.48	857.29	854.11	852.91	866.85	855.68	781.07

Table 10. Viscosities of CO₂+Ethanol Mixtures (g m s⁻¹)

conditions		mass percentage of ethanol							
<i>T</i> (K)	<i>P</i> (MPa)	0.00 %	2.50 %	4.60 %	7.10 %	10.00 %	23.80 %	45.40 %	100 %
313.16	15.00	0.0672	0.0701	0.0715	0.0732	0.0777	0.1012	0.1441	0.8942
	20.00	0.0772	0.0805	0.0818	0.0835	0.0860	0.1114	0.1596	0.9172
	25.00	0.0850	0.0888	0.0901	0.0919	0.0933	0.1202	0.1742	0.9406
	30.00	0.0931	0.0963	0.0977	0.0995	0.1003	0.1282	0.1873	0.9644
	35.00	0.1023	0.1031	0.1046	0.1065	0.1069	0.1355	0.1990	0.9886
323.16	15.00	0.0571	0.0594	0.0613	0.0639	0.0672	0.0878	0.1256	0.7589
	20.00	0.0688	0.0706	0.0719	0.0739	0.0767	0.0987	0.1395	0.7776
	25.00	0.0770	0.0793	0.0804	0.0822	0.0846	0.1077	0.1509	0.7965
	30.00	0.0851	0.0867	0.0879	0.0896	0.0920	0.1155	0.1605	0.8157
	35.00	0.0915	0.0935	0.0949	0.0966	0.0988	0.1226	0.1686	0.8353
333.16	15.00	0.0476	0.0502	0.0522	0.0548	0.0583	0.0785	0.1062	0.6502
	20.00	0.0598	0.0623	0.0640	0.0662	0.0684	0.0893	0.1222	0.6654
	25.00	0.0687	0.0711	0.0726	0.0745	0.0767	0.0980	0.1339	0.6809
	30.00	0.0738	0.0786	0.0800	0.0817	0.0842	0.1055	0.1431	0.6966
	35.00	0.0839	0.0855	0.0867	0.0884	0.0910	0.1122	0.1506	0.7126

Table 11. AAD (%) of the Equations Presented in the Section 2.2.

substance	Le Blanc	Wilke- Chang	Tang- Himmelbleau I	Holmes- Olander- Wilke	Tang- Himmelblau II	Perkins- Geankoplis	Lefler- Cullinam
benzyl acetate	21.60	17.31	10.61	17.31	7.96	12.51	15.79
2-phenylethyl acetate	23.48	24.12	7.29	13.89	5.38	9.30	12.34
3-phenylpropyl acetate	24.93	28.66	6.79	12.72	4.35	8.40	11.49
dibenzyl ether	22.63	29.25	7.31	14.37	5.75	9.57	12.48

Table 12. Complexation Constants, Calculated with Equation 15

substance	K_{AB}^{eq}	AAD (%)
benzyl acetate	15.0	4.20
2-phenylethyl acetate	11.1	4.37
3-phenylpropyl acetate	17.3	4.58
dibenzyl ether	8.5	4.40