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Infinite Dilution Diffusion Coefficients of Linalool and Benzene in Supercritical Carbon Dioxide

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In this work tracer diffusion coefficients of linalool in supercritical carbon dioxide were measured at 313.15, 323.15, and 333.15 K and pressures from (12−20) MPa using the chromatographic peak broadening technique. Linalool was chosen because it is one of the most important components of the flavor and fragrance of the citrus essential oil. The influence of pressure, temperature, and carbon dioxide density on the diffusion coefficients is examined, as well as the hydrodynamic behavior. The applicability of the following models is evaluated: Wilke−Chang, Hayduk−Minhas, He−Yu−Su, Catchpole−King, Dymond, and Liu−Silva−Macedo. Tracer diffusion coefficients of benzene were also measured and compared with literature values in order to survey the apparatus and procedure performance.

Introduction

Citrus oils are used in many industries involving flavor, beverages, food, cosmetics, soap, pharmaceuticals, chemicals, and insecticide. They generally contain over 90% (all mass) hydrocarbon terpenes and sesquiterpenes, about 5% oxygenated compounds such as aldehydes and alcohols, and less than 1% nonvolatile residues such as waxes and pigments.

Linalool, a terpenic alcohol (3,7-dimethyl-1,6-octadien-3-ol), is one of the most abundant oxygenated compounds responsible for the characteristic flavor and fragrance of citrus essential oils. Together with its esters, it is produced in large quantities. In addition, linalool is also used in the production of vitamin E.

Extraction and purification of citrus essential oil components can be accomplished from supercritical processes. The phase behavior and mass transfer of the solutes must be known accurately for reliable design, scale-up, and simulation of these supercritical units. However, diffusion coefficient data for terpenes in supercritical CO_2 are very scarce.

Supercritical fluid chromatography (SFC) can be used to determine equilibrium, kinetic, transport, and other relevant properties.[1] Giddings and Seager[2] and later workers developed the capillary peak broadening (CPB) technique, a SFC method, to measure binary diffusion coefficients at infinite dilution. It is based on the Taylor−Aris dispersion phenomenon.[3−6]

In this work we measured tracer diffusivities of linalool in supercritical carbon dioxide using the CPB technique. Linalool was studied at (313.15, 323.25, and 333.15) K and pressures from 12 to 20 MPa; diffusion coefficients of benzene were also measured from 12 to 16 MPa and compared with literature data in order to test the apparatus performance.

The influence of pressure, temperature, and carbon dioxide density on the diffusion coefficients is examined, as well as the hydrodynamic behavior. In addition, the applicability of several currently available correlation models is also evaluated.

Experimental Section

Chemicals. *Solutes*: linalool (Fluka, purity 97%); benzene (Merck, purity 99.7%). *Gases* (supplier, GASIN): hydrogen (purity 99.9995%); air (99.995%); carbon dioxide (purity 99.9999%; aluminum cylinder with dip tube and helium head pressure).

Equipment and Procedure. The experimental setup and the procedure are described in great detail by Silva and Macedo[7] and Filho et al.[8] in previous studies.

The equipment embodies a supercritical fluid chromatograph (SUPREX 200A) with a Rheodyne valve (loop of 0.2 μL), two empty columns (lengths 20.897 m and 12.481 m, and inner diameter 1.00 mm), a flame ionization detector at the column exit, and a fused silica capillary (length 27.2 cm and inner diameter 20 μm) located between the column and the detector.

The columns are two deactivated stainless steel tubes with an inner deposition of cadmium to avoid adsorption (supplier: Paralab S.A., Portugal). Hence, it is possible to deal with relatively polar compounds.

After the system temperature and pressure had reached the desired values, the flow system was allowed to equilibrate for 1−2 h. After thermal and hydrodynamic equilibria were established, the measurements started. The solute was introduced into the carbon dioxide stream by means of the above-mentioned injection valve. Four pulses of solute were injected onto the column per run, spaced by 20−30 min intervals to avoid any overlap of peaks. As suggested by Wells et al.,[9] the extent of peak tailing was

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Table 1. Experimental Conditions and Binary Diffusion Coefficients of Benzene and Linalool in Supercritical CO_2

P	T	ρ	$10^5\eta^b$	10^8D_{12}(benzene)	10^8D_{12}(linalool)
MPa	K	$kg·m^{-3}$	Pa·s	$m^2·s^{-1}$	$m^2·s^{-1}$
12	313.15	723.79	5.9347	1.631	1.154
12	323.15	595.45	4.4847	2.112	1.565
12	333.15	446.66	3.2891		1.985
14	313.15	767.87	6.5780	1.476	0.998
14	323.15	679.96	5.4074	1.723	1.289
14	333.15	571.79	4.3024		1.551
15	313.15	784.41	6.8418	1.294	
15	333.15	613.58	4.7101	2.046	
16	313.15	798.77	7.0819	1.297	0.943
16	323.15	728.05	6.0278		1.140
16	333.15	646.09	5.0561		1.347
18	313.15	822.94	7.5115		0.886
18	323.15	761.95	6.5173		1.112
18	333.15	694.20	5.6214		1.274
20	313.15	843.00	7.8948		0.799
20	323.15	788.42	6.9347		1.003
20	333.15	729.37	6.0817		1.140

[a] Data from NIST[12] [b]Fenghour et al.[13]

measured by means of an asymmetric factor defined as the ratio between the peak half-widths at 0.1 peak height. Following the recommendations of Sassiat et al.[10] and Liong et al.,[11] peaks with asymmetric factors higher than 1.3 were rejected for the calculations.

Experimental Conditions. The experiments were carried out at 313.15, 323.15, and 333.15 K and at 12, 14, 15, 16, 18, and 20 MPa. The corresponding densities, ρ, and viscosities, η, of CO_2 are listed in Table 1. Density values were obtained from NIST,[12] and viscosity values, from an empirical equation developed by Fenghour et al.[13]

The following conditions were observed: (1) The flow is laminar (Reynolds number obeys $24.2 < Re < 42.4$). (2) Secondary flow effects induced by centrifugal forces are negligible, since $4.8 < De\sqrt{Sc} < 8.4$ (advised: $De\sqrt{Sc} < 10$). Sc is the Schmidt number, $De = Re\sqrt{R_o/R_c}$ is called the Dean number, and R_o and R_c are the column and tubing coil inner radius, respectively. (3) The concentration profiles are Gaussian, since the Levenspiel and Smith[14] criterion was always verified, $0.0000472 < D/U_oL < 0.000186$ (advised: $D/U_oL < 0.01$), where L is the length of the column, D is a dispersion coefficient defined by $D = D_{12} + R_o^2U_o^2/48D_{12}$, U_o is the average linear velocity of the solvent, and D_{12} is the tracer diffusion coefficient. This result is corroborated by the good fittings obtained with normal curves (correlation coefficients from 99.809% up to 99.998%) and by the asymmetric factors, which range from (1.01 to 1.19). We decided to start the measurements at 12 MPa to increase the solvent power of CO_2, to reduce even more the possibility of adsorption by the inner walls of the columns. In a previous work[7] our experiments were also carried out at 8 and 10 MPa, since the ethers studied do not create such problems.

Figure 1 illustrates a chromatogram of the linalool−CO_2 system obtained with the small column at 333.15 K and 16 MPa.

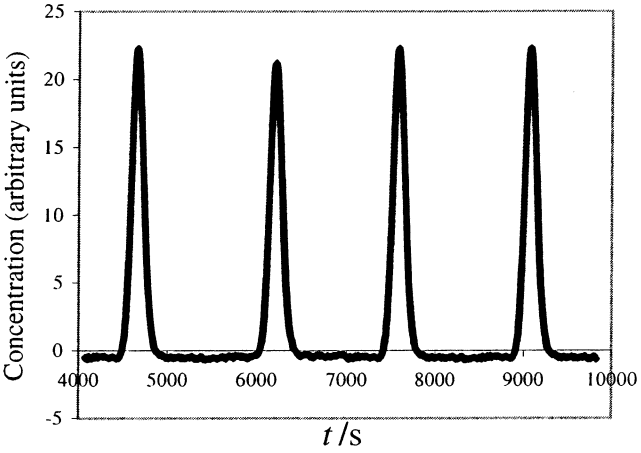

Figure 1. Chromatogram of the linalool−CO_2 system obtained with the small column ($L = 12.481$ m) at $T = 333.15$ K and $P = 16$ MPa.

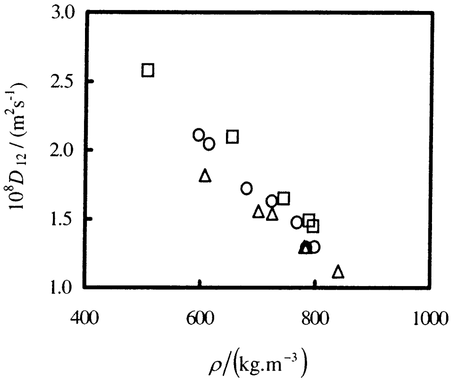

Figure 2. Diffusion coefficients of benzene as a function of carbon dioxide density: ○, this work; □, Sassiat et al.;[10] △, Bueno et al.[15]

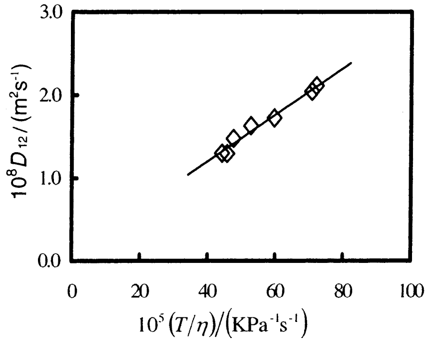

Figure 3. Diffusion coefficients of benzene plotted in Stokes−Einstein coordinates.

Results and Discussion

Tracer Diffusion Coefficients of Benzene. The data obtained for diffusion coefficients of benzene in supercritical CO_2 are presented in Table 1. Figure 2 shows a comparison between those values and others available in the literature[10,15] in the temperature range (313.15−333.15) K and at pressures from 12 up to 200 MPa. Good agreement with both source data series can be observed, which confirms the reliability of our experimental setup and procedure. All data exhibit similar density dependence. Figure 3 also presents the diffusion coefficients of benzene in Stokes−Einstein coordinates (D_{12} against T/η). A slight hydrodynamic deviation is verified by a small intercept of the extrapolated line.

Tracer Diffusion Coefficients of Linalool. The experimental diffusivities are listed in Table 1 and range from $(0.799 \text{ to } 1.985) \times 10^{-8}\ m^2·s^{-1}$. Spicka et al.[16] published two values at 333.15 K that are comparatively smaller than those obtained in this work: $D_{12} = 0.87 \times 10^{-8}\ m^2·s^{-1}$ at 9.64 MPa and $D_{12} = 0.80 \times 10^{-8}\ m^2·s^{-1}$ at 19.61 MPa. However, we consider our data of good quality, since the experimental data obtained in this study for benzene prove the good performance of our apparatus and procedure, and

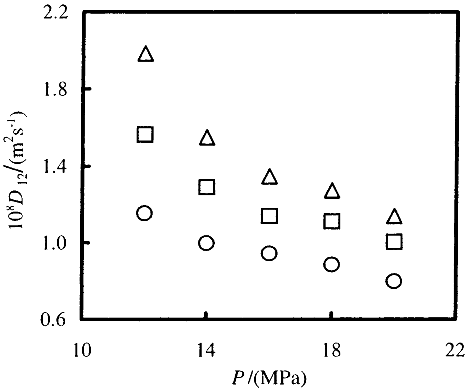

Figure 4. Diffusion coefficients of linalool as a function of pressure at constant temperature: ○, 313.15 K; □, 323.15 K; △ 333.15 K.

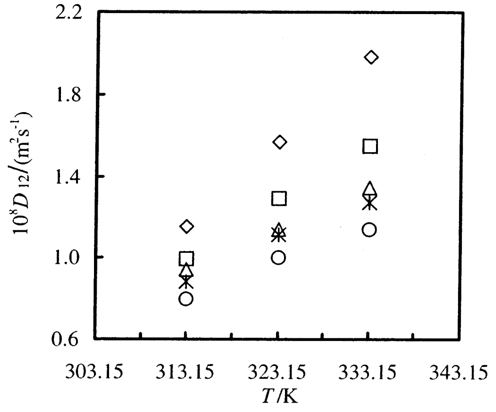

Figure 5. Diffusion coefficients of linalool as a function of temperature at constant pressure: ◇, 12 MPA; □, 14 MPa; △, 16 MPa; ∗, 18 MPa; ○, 20 MPa.

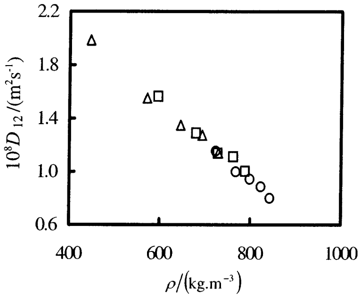

Figure 6. Diffusion coefficients of linalool as a function of carbon dioxide density: ○, 313.15 K; □, 323.15 K; △, 333.15 K.

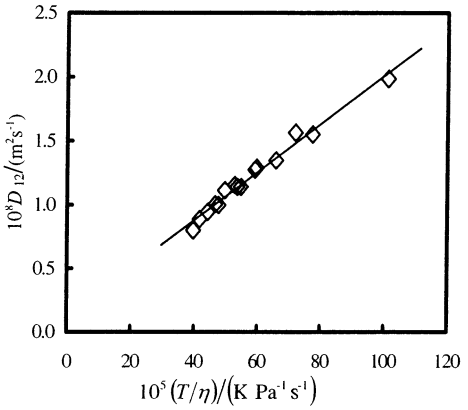

Figure 7. Diffusion coefficients of linalool plotted in Stokes–Einstein coordinates.

Table 2. Data for Pure Substances

property[a]	CO_2	linalool
M/kg·kmol^{-1}	44.0098	154.254
T_c/K	304.21[b]	645.8[g]
P_c/MPa	7.383[b]	2.595[g]
10^3V_c/m^3·kmol^{-1}	94.0[c]	558[g]
T_{bp}/K	202.98[d]	472.0[h]
10^3V_{bp}/m^3·kmol^{-1}	33.32[e]	218.72[i]
σ^{LJ}/Å	3.26192[f]	6.40654[j]
(ϵ^{LJ}/k)/K	500.71[f]	499.85[j]

[a] M = molecular weight, P_c = critical pressure, T_c = critical temperature, V_c = molar critical volume, T_{bp} = temperature at the normal boiling point, V_{bp} = volume at the normal boiling point, σ^{LJ} = Lennard-Jones molecular diameter, ϵ^{LJ}/κ = Lennard-Jones energy parameter. [b] DIPPR.[24] [c] Mathews.[25] [d] Average of the values estimated using the Joback method[18] and Guldberg's rule: $T_{bp} = {}^2/_3T_c$. [e] Estimated by the Tyn–Calus expression.[18] [f] Liu et al.[26] [g] Average of values estimated by the Ambrose and Joback methods.[18] [h] Perry and Green.[27] [i] Average of values estimated by the Tyn–Calus expression and the Le Bas method.[18] [j] Silva et al.[28]

Table 3. Calculation Results for Linalool

model	AAD%	model	AAD%
Wilke–Chang	8.07	Dymond[a]	4.03
Hayduk–Minhas	4.11	TLSM-en[b]	3.51
He–Yu–Su	3.53	TLSM-d[c]	3.49
Cathpole–King	3.59		

[a] Using the B parameter ($B = 1.3508 \times 10^{-7}$) and the V_D parameter ($V_D = 14.10$). [b] Using the binary parameter adjusted (κ^{en} = 0.371 301 8). [c] Using the binary parameter adjusted (κ^{d} = 0.083 604 6).

because all criteria that this work imposes are totally satisfied.

The influence of state and solvent properties on the diffusion coefficient is shown in Figures 4–7.

Figure 4 shows 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.[7–9,17]

From Figure 5 a high dependence of D_{12} on temperature at isobaric conditions is observed. This behavior is more pronounced at low pressures and is in exact agreement with that seen in other works.[7–10,15,17]

Figure 6 illustrates a large dependence of D_{12} on density at constant temperature. In the density range studied this relationship is approximately linear. The linalool diffusivities against T/η are represented in Figure 7, together with a liner fitting. The small intercept shows a slight deviation from the hydrodynamic behavior. Both figures follow the results obtained by several authors.[7–10,15,17]

Modeling the Diffusion Data. The accuracy of several models is examined with the tracer diffusivities of linalool measured in this work: (i) four purely predictive equations (the hydrodynamic correlations of Wilke–Chang and Hayduk–Minhas,[18] the free volume model of He–Yu–Su,[19] and the Catchpole–King correlation[20]) and (ii) three equations with adjustable parameters (the free volume model of Dymond[21,22] with two parameters and the two Lennard-Jones correlations of Liu et al.[23] ($TLSM_{en}$ and $TLSM_d$), which involve just one binary parameter (for energy and diameter corrections, respectively)).

In Table 2 all data necessary for the calculations are listed, and Table 3 contains the absolute average deviations (AAD%) obtained. According to Table 3 all models perform satisfactorily. The $TLSM_d$ model achieves the best result, and the Wilke–Chang model, the worst one.

Conclusions

This work presents new tracer diffusion coefficients of benzene and linalool in supercritical carbon dioxide at three temperatures (313.15, 323.25, and 333.15 K) and five pressures (12, 14, 16, 18, and 20 MPa).

The linalool binary diffusivities measured range from (0.799 to 1.985) × 10^{-8} $m^2 \cdot s^{-1}$. The dependencies on state and CO_2 properties are in good agreement with those of other works in the field. The relationship between D_{12} and CO_2 density is nearly linear under the experimental conditions. The Stokes−Einstein behavior was also observed.

The seven models adopted to estimate linalool diffusivities in CO_2 give good results. The $TLSM_d$ model exhibits the best representation, and the Wilke−Chang equation, the worst prediction.

Literature Cited

(1) Sunol, S. G.; Mierau, B.; Serifoglu, I.; Sunol, A. K. *Estimation of Physicochemical Properties Using Supercritical Fluid Chromatography. Supercritical Fluids—Extraction and Pollution Prevention*; ACS Symposium Series No. 670; American Chemical Society: Washington, DC, 1997; p 188.
(2) Giddings, J. C.; Seager, S. L. Rapid Determination of Gaseous Diffusion Coefficients by Means of a Gas Chromatography Apparatus. *J. Chem. Phys.* **1960**, *33*, 1579.
(3) Taylor, G. Dispersion of Solute Matter in Solvent Flowing Slowly Through a Tube. *Proc. R. Soc. London* **1953**, *219*, 186.
(4) Taylor, G. The dispersion of Matter in Turbulent Flow Through a Pipe. *Proc. R. Soc. London* **1954a**, *223*, 446.
(5) Taylor, G. Conditions under which Dispersion of a Solute in a Stream of Solvent can be used to Measure Molecular Diffusion. *Proc. R. Soc. London* **1954b**, *225*, 473.
(6) Aris, R. On the Dispersion of a Solute Flowing Through a Tube. *Proc. R. Soc. London* **1956**, *67*, 235.
(7) Silva, C. M.; Macedo, E. A. Diffusion Coefficients of Ethers in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1998**, *37*, 1490.
(8) Filho, C. A.; Silva, C. M.; Quadri, M. B.; Macedo, E. A. Tracer Diffusion Coefficients of Citral and d-Limonene in Supercritical Carbon Dioxide. *Fluid Phase Equilib.*, in press.
(9) Wells, T.; Foster, N. R.; Chaplin, R. P. Diffusion of Phenylacetic Acid and Vanillin in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 927.
(10) Sassiat, P. R.; Mourier, P.; Caude, M. H.; Rosset, R. H. Measurement of Diffusion Coefficients in Supercritical Carbon Dioxide and Correlation with the Equation of Wilke and Chang. *Anal. Chem.* **1987**, *59*, 1164.
(11) Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion in Supercritical Fluids. *J. Supercrit. Fluids* **1991**, *4*, 91.
(12) NIST. *NIST Standard Reference Database 69*—February 2000 (Release: NIST Chemistry WebBook), 2000.
(13) Fenghour, A.; Wakeham, W. A.; Vesovic, V. The Viscosity of Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1998**, *27*, 31.
(14) Levenspiel, O.; Smith, W. K. Notes of the Diffusion Type Model for Longitudinal Mixing of Fluids in Flow. *Chem. Eng. Sci.* **1957**, *6*, 227.
(15) Bueno, J. L.; Suárez, J. J.; Dizy, J.; Medina, I. Infinite Dilution Diffusion Coefficients: Benzene Derivatives as Solutes in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1993**, *38*, 344.
(16) Spicka, B.; Alessi, P.; Cortesi, A.; Kikic, I.; Macnaughton, S. *Diffusion Coefficients of Terpenes in Supercritical CO_2*; Proceedings of the 3rd International Symposium on Supercritical Fluids, Strasbourg, France; 1994; Vol. 1, p 301.
(17) Swaid, I.; Schneider, G. M. 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. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 969.
(18) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: Singapore, 1988.
(19) He, C.; Yu, Y.; Su, W. Tracer Diffusion Coefficients of Solutes in Supercritical Solvents. *Fluid Phase Equilib.* **1998,** *142*, 281.
(20) Catchpole, O. J.; King, M. B. Measurement and Correlation of Binary Diffusion Coefficients in Near Critical Fluids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1828.
(21) Chen, S. H.; Davis, H. T.; Evans, D. F. Tracer Diffusion in Polyatomic Liquids. III. *J. Chem. Phys.* **1982**, *77*, 2540.
(22) Dymond, J. H. Corrected Enskog Theory and the Transport Coefficient of Liquids. *J. Chem. Phys.* **1974**, *60*, 969.
(23) Liu, H.; Silva, C. M.; Macedo, E. A. New Equations for Tracer Diffusion Coefficients of Solutes in Supercritical and Liquid Solvents Based on the Lennard-Jones Fluid Model. *Ind. Eng. Chem. Res.* **1997**, *36*, 246.
(24) DIPPR. *DIPPR Tables of Physical and Thermodynamics Properties of Pure Compounds*; AIChE: New York, 1998.
(25) Mathews, J. F. The Critical Constants of Inorganic Substances. *Chem. Rev.* **1972**, *72*, 71.
(26) Liu, H.; Silva, C. M.; Macedo, E. A. Unified Approach to the Self-Diffusion Coefficients of Dense Fluids over Wide Ranges of Temperature and Pressure—Hard-Sphere, Square-Well, Lennard-Jones and Real Substances. *Chem. Eng. Sci.* **1998**, *53*, 2403.
(27) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 6th ed.; McGraw-Hill: New York, 1984.
(28) Silva, C. M.; Liu, H.; Macedo, E. A. Models for Self-Diffusion Coefficients of Dense Fluids, Including Hydrogen-Bonding Substances. *Chem. Eng. Sci.* **1998,** *53*, 2423.

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