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Binary diffusion coefficients for 2,3-dimethylaniline, 2,6-dimethylaniline, 2-methylanisole, 4-methylanisole and 3-nitrotoluene in supercritical carbon dioxide

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ABSTRACT

The measurement and correlation of the experimental binary diffusion coefficients of 2,3-dimethylaniline, 2,6-dimethylaniline, 2-methylanisole, 4-methylanisole and 3-nitrotoluene in supercritical carbon dioxide is reported. Results were obtained using the Taylor-Aris dispersion technique, at 313, 323, and 333 K, and in a pressure range from 15.0 to 35.0 MPa. The diffusivity experimental data were correlated with temperature, pressure and carbon dioxide density and viscosity. Moreover, the experimental results were compared with the values estimated by several semiempirical equations.

1. Introduction

Supercritical fluid solvents are now in widespread use for a large variety of applications. They have a liquid-like solvating strength and gas-like transport properties which make them a unique medium for extractions, chemical reactions, or particle generation processes. Selectivity can be achieved by selecting the appropriate pressure, temperature and modifier conditions, to enable the solvating power to be adjusted. The high diffusivity and low viscosity of supercritical fluids ensures rapid sample penetration and extraction [1].

Supercritical carbon dioxide is by far the most important supercritical fluid. The demand for green technologies is continually increasing due to the growing awareness of alimentary, environmental and toxicity risks. Supercritical technologies have benefited from this interest, especially in the alimentary, oil and pharmaceutical industries. Carbon dioxide is the most common supercritical fluid, mainly because it is easy to handle, it is inert, non-toxic, non-flammable, and has convenient critical coordinates.

As a first step towards developing any supercritical fluid technology, several mixture properties need to be determined, including the solubility and transport properties of the solutes in the supercritical fluid at the operating conditions. Several efforts have been focussed on measuring these physicochemical parameters for chemical compounds representative of families of homologues and on defining thermodynamic approaches that might facilitate the description, and/or prediction, of the properties over a reasonably wide range of temperatures and pressures. For example, diffusion coefficients and other experimental data in supercritical carbon dioxide have been reviewed in recent literature [2]. However, more experimental measurements are required for essential modeling and design.

Recently, some studies have been carried out to improve the understanding of transport properties in supercritical fluids. The role of attractive forces in mutual diffusion of phenol in both liquid and supercritical CO_2 has been investigated by Coelho et al. [3]. The experimental data from molecular simulations and the theoretical results agree fairly well with the experimental results. Calculation of transport properties using the inverted potential has been discussed by Papari [4]. Rather accurate correlations for viscosity and thermal conductivity have been obtained. The accuracies are to within 1% for viscosity and 3% for thermal conductivity. Ghayeb et al. [5] have been presented a new method for the calculation of the viscosity of supercritical fluids at high temperatures and pressures based on the modified Enskog theory. The accuracy of the calculated viscosity is about 0.3%. A model for representing the viscosity of supercritical pure fluids over a wide range of conditions has been proposed by Zabaloy et al. [6]. The average absolute-value relative deviations are less than or equal to 7% in most cases. In an extensive computer simulation study, Meier et al. [7–9] have been

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Nomenclature

a_P	fitting constant of Eq. (1)
a_T	fitting constant of Eq. (2)
a_η	fitting constant of Eq. (5)
a_ρ	fitting constant of Eq. (4)
AAD	Average Absolute Deviation
b_P	fitting constant of Eq. (1)
b_T	fitting constant of Eq. (2)
b_η	fitting constant of Eq. (5)
b_ρ	fitting constant of Eq. (4)
BIAS	Average Deviation
c	fitting constants of Eq. (3)
De	Dean number
D_{AB}	binary diffusivity at infinite dilution
F_D	corrective function
$g(\sigma)$	radial distribution function
h_D	rotational-translational coupling parameter
k	Boltzmann constant
m	molecular mass
M	molar mass
n	number density
P	pressure
RHS	Rough Hard Sphere
RMSD	Root Mean Squared Deviations
Sc	Schmidt number
SE	Stokes–Einstein
T	absolute temperature
V	molar volume

Greek letters

η	viscosity
ρ	density
σ	molecular diameter
ω	acentric factor

Subscripts

A	solute
AB	solute–solvent mixture
b	boiling point
B	solvent
c	critical point

Superscripts

eff	effective (temperature dependent)

determined transport coefficients of the Lennard-Jones model fluid with high accuracy. The temperature and density dependences of viscosity, self-diffusion and bulk viscosity were characterized over a wide range of fluid states. González et al. [10] have extended two corresponding states models to the diffusion in supercritical carbon dioxide. An equation for self-diffusion coefficients of hard-spheres, Lennard-Jones systems and real fluids has been obtained by Suárez-Iglesias et al. [11], which is capable to correlate an extensive database in the full-density range.

In this study, the diffusion coefficients of 2,3-dimethylaniline, 2,6-dimethylaniline, 2-methylanisole, 4-methylanisole, and 3-nitrotoluene in supercritical carbon dioxide were measured by the Taylor-Aris dispersion method. The influence of pressure, temperature, density and viscosity on the binary diffusion coefficients was investigated. The experimental data were compared with those estimated by employing any of the models based on the Stokes–Einstein formula or models based on the Rough-Hard-Sphere (RHS) equation. The effect of molecular geometry was also investigated by observing the diffusivities of the solutes.

These substances have been selected because the lack of diffusivities concerning simple benzene derivatives with the amine, nitro and methoxy groups reported in the literature. Moreover, all of these existing bibliographic data were due to some of us [2,12–15].

2. Experimental

The experimental diffusion coefficients were measured in a Hewlett-Packard supercritical fluid chromatograph (SFC), model G1205A, which was slightly modified. The HP SFC system consists of a pumping module, a column oven, an injection valve, a mass flow sensor, specially chosen detectors and SFC ChemStation software [10,12,13,16]. Fig. 1 shows the main elements of the employed apparatus.

The oven module can accommodate fused silica capillary and standard HPLC columns. The HP SFC uses both gas and liquid phase detectors. In the present work, this unit uses a multiple wavelength UV detector (MWD). The HP SFC has an electrothermally cooled reciprocating pump to supply supercritical fluids to the system. The pump has a feedback control, which compensates for fluid compressibility, minimizes ripple pressure, and provides more reproducible results. In addition, the use of a reciprocating pump eliminates the inconvenience associated with having to refill the syringe pumps. The variable restrictor is a programmable, backpressure control device located inside the pump module. It consists of a pressure transducer and nozzle, which opens and closes in order to release the mobile phase and control pressure. The SFC ChemStation consists of a PC and HP SFC software. The SFC ChemStation allows instrument control and data handling on a Microsoft® Windows-based platform. The mass flow sensor is a device that is located inside the pumping module.

Carbon dioxide was pressurized and passed into the diffusion column. The temperature and pressure were measured to accuracies of ±1 K and ±0.1 MPa, respectively. After the desired temperature and pressure were attained, a 0.2 μl portion of solute was loaded into the injection loop. This pulse of solute develops towards a Gaussian profile, which variance is related with the diffusion coefficient, as explained elsewhere [10,17]. To ensure the accuracy of the experimental data, the concentration curves were measured after 60 min, at which point the system had reached equilibrium. The diffusion column was a stainless steel coiled tube with an inner diameter of 0.762 mm and a length of 30.48 m. Zero dead-volume fittings were used to eliminate peak broadening resulting from fitting effects. All diffusion coefficient values represent mean values of at least seven samplings. The percent relative standard deviations of the measurements were within an error margin of ±2%.

The carbon dioxide used in this work was supplied by Air Liquide and had a purity of 99.998%. 2,3-Dimethylaniline (purity >99%), 2,6-dimethylaniline (>98%), 2-methylanisole (>98%), 4-methylanisole (>99%), and 3-nitrotoluene (>99%) were obtained from Merck (synthesis grade). These chemicals were used as received without further purification.

The diffusion coefficients were calculated by absorbance measurements at three wavelengths for each compound: 305, 307, and 309 nm for 2,3-dimethylaniline; 303, 305, and 307 for 2,6-dimethylaniline; 237, 239, and 241 for 2-methylanisole; 238, 240, and 243 for 4-methylanisole; and 329, 333, and 340 for 3-nitrotoluene. No tailing was observed, and the peaks were symmetrical in all the runs.

Several factors may contribute to error with this technique. Adsorption of the solute on the column wall can lead to peak tailing (non-Gaussian curves) and pipe coiling can cause secondary