



Determination of diffusion coefficients by supercritical fluid chromatography: Effects of mobile phase mean velocity and column orientation

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ABSTRACT

The supercritical fluid (SCF) chromatographic technique based on the Taylor dispersion theory has been widely applied in determination of diffusion coefficients of various organic compounds in SCFs. This study was aimed to understand impacts of mobile phase mean velocity (MPMV) and column orientation on diffusion coefficient measurements. The benzene/SCCO₂ system was investigated. Experiments were carried out at 40 and 60 °C and 9–15 MPa over a wide range of CO₂ densities at varying MPMV and repeated in two column orientations, vertical and horizontal. It was found that both MPMV and column orientation significantly affected measurements of diffusion coefficients in SCFs. When the column was installed vertically, apparent diffusion coefficients obtained at relatively low CO₂ density (<580 kg/m³) increased with increasing MPMV over the entire velocity ranges. This results in a conclusion that diffusion coefficients cannot be accurately determined under these conditions using a vertically installed column. Under all other conditions, as MPMV increased, apparent diffusion coefficients initially increased, then remained constant, and finally increased again. The initial increase of apparent diffusion coefficients was associated with significant decline of curve-fitting errors, which indicates that the buoyancy effects are non-negligible and will cause larger errors. Accordingly, a new generalized D_{12} – U diagram comprised of three regions is proposed. Column orientation affected diffusion coefficient measurements mainly by enhancing or weakening the buoyancy effects. When the column was installed vertically, the buoyancy effects were enhanced, leading to lower apparent diffusion coefficients, especially when CO₂ density was relatively low. In addition, it was found that when CO₂ density was below ~580 kg/m³, diffusion coefficients obtained when the column was horizontally installed were higher than those obtained when the same column was vertically installed. When CO₂ density was above that value, opposite outcomes resulted. Finally, the horizontal orientation of a diffusion column is recommended for diffusion coefficient measurements by the SCF chromatographic technique, especially when densities of SCFs are relatively low.

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1. Introduction

Supercritical fluids (SCFs) have been widely investigated as reactants and/or green solvents due to their unique tunable thermophysical properties since late 1980s [1]. Their applications have been expanded since then, as Kiran et al. [1] stated, “in a very dramatic way into inorganic materials, polymers, emulsions, biomedical applications, hydrothermal processes, reactions, catalysis, environmental remediation, alternative energy, nanotechnology and hybrid materials”. Knowledge of thermophysical properties of SCFs and other species involved in SCF systems is crucial to advancing the SCF technology and to developing SCF processes. Binary diffusion coefficients are one such property that

needs further investigation. Although binary diffusion coefficients in SCFs have been studied since the 1960s [2], experimental data are still very limited [3]. Moreover, the accuracy of data from various sources has seldom been justified. A comparison of diffusion coefficients of benzene in supercritical carbon dioxide (SCCO₂) from various sources showed large variations especially when the density of CO₂ is below the critical value [4]. These variations largely resulted from experimental errors. Therefore, a better understanding of those aspects that influence uncertainties of measurements of binary diffusion coefficients in SCFs is of practical importance.

Moreover, among fluid thermophysical properties, molecular binary diffusion coefficients are less understood than others due to both theoretical challenges and experimental difficulties. The accuracy of estimates for gases based on the Chapman–Enskog theory is around 10%, while that for liquids based on the Stokes–Einstein equation or its empirical correlations is about 20% [5]. These estimates help to solve only the routine problems, as Cussler [5]

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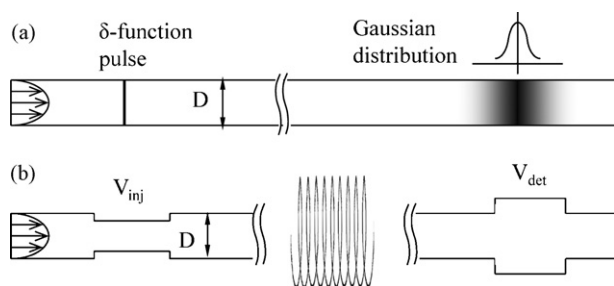


Fig. 1. Comparison of ideal and real Taylor dispersion experiments for diffusion coefficient measurements. (a) Straight cylindrical tube; (b) coiled cylindrical tube; D : diameter; V_{inj} : injection volume; V_{det} : detection volume.

pointed out. Limitations exist, for example, in the field of diesel engine combustion where mass diffusion can limit the combustion rates [6], and the information on mass diffusion coefficients is less reliable [7]. Therefore, the current study is also intended to make contributions to advance the fundamentals of fluid thermophysical properties.

Among all experimental techniques [5] developed to date for determination of diffusion coefficients, the chromatographic technique [2,8–11], also known as the peak broadening technique, has been mostly applied in SCF systems. Recent applications of this technique include determination of diffusion coefficients of various organic compounds in SCCO_2 [4,12,13]. This technique is based on the ideal Taylor dispersion model developed by Taylor [14,15] and further extended by Aris [16]. Fig. 1 shows schematically the difference between the ideal (Fig. 1a) and the real (Fig. 1b) Taylor dispersion experiments for diffusion coefficient measurements. In the ideal experiment, a δ -function type solute pulse is introduced in a laminar flow inside a straight cylindrical pipe. Under the combined action of bulk convection and molecular diffusion, the pulse disperses symmetrically, forming a Gaussian distributed concentration profile. In practice, however, a coiled dispersion column is usually applied to minimize space usage and for better temperature control. Moreover, an approximately rectangular pulse is injected instead of a δ -function type one, and the concentration of the effluent at the end of tube is averaged over a finite detection volume. These departures of the real experiment from the ideal one result in significant experimental uncertainties. Alizadeh et al. [17] classified and examined these departures in four groups: sample injection, diffusion column geometry, concentration measurement, and fluid properties. In addition, flow conditions and P – T control [18], dead volume [18], and wall adsorption [19] may also contribute to experimental uncertainties.

The main objective of this study was to understand impacts of flow conditions and diffusion column geometry, more specifically, mobile phase mean velocity (MPMV) and column orientation when a coiled column is used. Other factors mentioned in the preceding paragraph are beyond the scope of this work.

MPMV is an important parameter that practically affects diffusion coefficient measurements, although diffusion coefficients are theoretically independent of MPMV. A typical relationship between apparent (or measured) diffusion coefficients and MPMV is shown in Fig. 2 [18,20–23]. As MPMV is reduced from a high level, the apparent diffusion coefficient decreases initially and then reaches a constant value which is the real value of diffusion coefficient. The increase in apparent diffusion coefficient with increasing MPMV is known as a consequence of the secondary flow effects due to tube coiling. Therefore, accurate diffusion coefficients can be determined only within a limited range of MPMV. This limited range within which apparent diffusion coefficients are independent of MPMV is defined in this work as the *optimal velocity range* (OVR). Various OVRs were reported in the literature [4,18,21–26]. How-

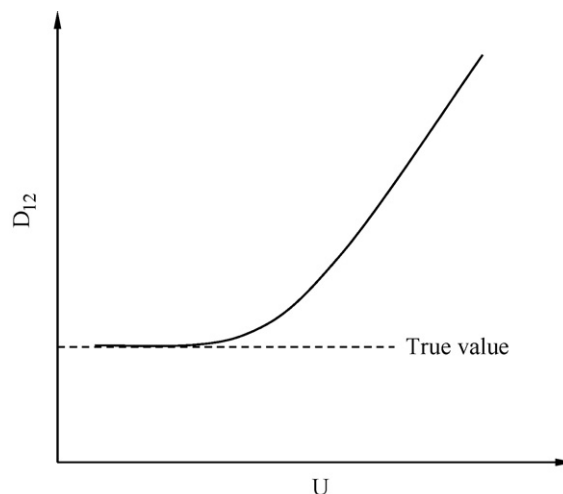


Fig. 2. Typical relationship between apparent diffusion coefficient and MPMV.

ever, no information is available about whether or not the OVR is affected by other operation conditions.

It is well-known that coiling of a tube brings centrifugal forces on flowing fluids, which creates secondary flows that can influence the dispersion process. The effect of tube curvature on the laminar dispersion of solute in a circular tube has been extensively studied [17,27–29]. Erdogan and Chatwin [27] treated the problem in a similar analytical way as Taylor [14,15] did for straight tubes using the velocity distribution of Dean [30,31] and predicted that the dispersion coefficient is always reduced by the curvature for all common liquids and most gases if the radius of the curvature is sufficiently large. Nunge et al. [28], employing the velocity distribution of Topakoglu [32], extended the previous analysis to small curvature and found that the dispersion coefficient may be increased substantially by curvature in low Reynolds number flows. The authors [28] attributed this behavior to the opposing impacts of the asymmetric axial velocity distribution, which tends to increase dispersion, and the secondary flow, which decreases the dispersion by creating a transverse mixing. Employing results of the previous study, Alizadeh et al. [17] established conditions under which the effects of curvature are negligible, which provided a useful guide for the design of experiment for diffusivity measurements. A dimensionless group, one that is the product of the Dean number (De) and the square root of the Schmidt number (Sc), $De\sqrt{Sc}$, has been successfully formulated and applied to characterize the effect of curvature [4,17,18].

All analytical studies referred in the preceding paragraph were based on the assumptions that the mobile phase is incompressible and the density of the solute/mobile phase mixture is constant and independent of solute concentration. When the density of the solute differs from that of the mobile phase and the density of the mixture depends on solute concentration, which is inevitably encountered in most SCF systems, the problem becomes much more complicated. Density gradients induce buoyancy forces which may cause significant uncertainties in diffusivity measurements. Reejhsinghani et al. [33] observed the impact of density difference on dispersion in horizontal tubes. Erdogan and Chatwin [27] also studied this issue and concluded that the effect of buoyancy forces is related to the magnitude of Peclet numbers. Buoyancy effects have also been recognized in other transport property measurements [34].

Coiled columns used in diffusion coefficient experiments were usually installed either horizontally [12,20,24,35,36] or vertically [4,18,25,26,37] depending on the temperature control instrument used. Less attention, however, has been given to the understanding

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