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Measurement of Diffusion in Fluid Systems: Applications to the Supercritical Fluid Region

Thomas J. Bruno*
National Institute of Standards and Technology, Boulder, Colorado 80303

In this article, the experimental procedures that are applicable to the measurement of diffusion in supercritical fluid solutions will be reviewed. This topic is of great importance to the proper design of advanced aircraft and turbine fuels, since the fuels on these aircraft may sometimes operate under supercritical fluid conditions. More specifically, we will consider measurements of the binary interaction diffusion coefficient D_{12} of a solute (species 1) and the solvent (species 2). In this discussion the supercritical fluid will be species 2, and the solute, species 1, will be at a relatively low concentration, sometimes approaching infinite dilution. After a brief introduction to the concept of diffusion, we will discuss in detail the use of chromatographic methods, and then briefly treat light scattering, nuclear magnetic resonance spectra, and physical methods.

Nomenclature

D = general form of the diffusion coefficient
D_{aa} = self diffusion coefficient
D_{12} = binary interaction diffusion coefficient
De = Dean number
e = elliptical eccentricity
H = height equivalent to a theoretical plate
J_{iz} = flux of matter passing a unit area due to diffusion
L = length of diffusion tube
R = radius of diffusion tube coil
Re = Reynolds number
r = internal radius of diffusion tube
Se = Schmidt number
u = average velocity of carrier fluid in diffusion tube
δ = general form of the Dirac delta function
η = fluid viscosity
ρ = fluid density
σ = square root of variance of Gaussian curve
ω = ratio of radius of tube coil to the inside radius of the tube

Introduction

THE concept of diffusion stems from a central principal of physical and chemical phenomena: the natural tendency to establish uniformity in a fluid phase. By uniformity, we mean the equality of the expectation value (i.e., the measured or calculated result) of a particular property as it exists through a volume of fluid. We have the intuitive conviction that a local nonuniformity (or perturbation) in a fluid, over and above that produced by natural molecular motions, is an unstable and unsustainable situation. In fact, the uniform system is in its state of minimum energy, and is therefore the most stable. The types of nonuniformities that may exist include perturbations in temperature, pressure, component concentration, or even a material-dependent response to the effects of external force fields. The general topic of transport phenomena is the study of such perturbations and nonuniformity in fluids.[1]

In this article, we will focus on only one specific aspect of transport phenomena, that of diffusion. We will further confine ourselves to the consideration of experimental measurements of diffusion in supercritical fluid systems under a constant temperature and pressure, with no external applied fields other than those required for measurement.

There are many ways in which nonuniformity in composition can arise in a fluid phase. A local chemical reaction in a uniform fluid can occur. We can envision this happening when a potentially reactive fluid wets a potentially catalytic or hot surface, and a reaction occurs on the surface. This is a major consideration in the design of high-performance aircraft. In future aircraft such as the advanced tactical fighter (ATF), the fuel will serve the dual purpose of providing propulsion and providing a heat sink for leading-edge surfaces. These surfaces undergo significant heat load due to frictional heating by the air slipstream, and the fuel will be circulated in heat exchangers in contact with these surfaces to relieve some of this heat overhead. During the heat sink cycle(s), the fuel fluid will often be in the supercritical fluid state (i.e., above the critical temperature and critical pressure for the mixture). After the heat sink cycle(s), the fuel is pumped into the turbines to provide propulsion. Clearly, residence time in the heat exchangers is a major factor that controls the relative severity of the thermal stress that the fuel undergoes. During a typical combat mission, the most thermal stress to the fuel will occur on the return trip, after the engagement over the target. During this phase of the mission, we can expect the aircraft surfaces to be hot, and the fuel flow rate into the engines to be relatively low. Under these conditions, chemical reactions of the fuel mixture are a significant possibility. The reaction product will then be released in the locality of the surface, creating the localized compositional nonuniformity.

Another process that can be considered is when a solvent is brought into contact with a solute located in a defined but nonuniform matrix. The solvation of caffeine in a matrix of coffee beans provides such an example. The caffeine, which is captive in the plant matter, is dissolved by a volume of solvent. Initially, a higher concentration of caffeine will exist in the vicinity of the matrix.

We can define the diffusion process as the net movement (or transport) of material within a single phase. While diffusion across an interface separating two phases (such as the boundary between a liquid and its vapor head space) can be considered, it is a complication that will not be treated here. In our mental concept of diffusion, material (or mass) transport occurs without mixing (mechanical or convective), but rather in response to 1) the natural minimization of the overall chemical potential of the system, and 2) the kinetic influence of random molecular motion. Thus, the diffusion of one mol-

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*Group Leader, Thermophysics Division.

ecule into a field composed of other molecules has both a thermodynamic and a kinetic contribution. The flux of matter (the number of molecules passing a unit area) due to diffusion is proportional to the concentration gradient in the direction normal to the area. The flux (in the *z* direction) is represented as J_{iz}, and the concentration gradient is $\mathrm{d}n_i/\mathrm{d}z$. The proportionality constant between the flux and the concentration gradient is the diffusion coefficient, or the diffusivity D, represented by Fick's law[1]:

$$J_{iz} = -D\frac{\mathrm{d}n_i}{\mathrm{d}z} \tag{1}$$

The nomenclature used in describing diffusion should be discussed, since it can be a source of much confusion. D_{12}, described earlier in the examples on jet fuels and caffeine, is the diffusion coefficient that describes the diffusion of component 1 (the solute) into component 2 (the solvent). This is also commonly called the mutual diffusion coefficient, the binary diffusion coefficient, or the interaction diffusion coefficient, and it refers only to a binary system. It should be noted in this context that sometimes a solution that is more complicated than a simple binary is approximated as a binary mixture. The effect of this approximation must be considered on a case by case basis in evaluating the validity of using D_{12} in these instances. This diffusion coefficient is perhaps of the most importance because of its usefulness in describing mass transport in engineering applications such as extraction.[2] This is commonly expressed in the dimensionless Schmidt number (since later discussion in this article will involve this quantity, we will postpone its definition and description until that time). Tracer diffusion coefficients refer to the diffusion of a labeled component into a homogeneous mixture. D_{aa} of a molecule describes the flux of a particular molecule through a field made up of the same molecules. This term is different from the others in that it is purely kinetic; there is no chemical potential driving the process.

Experimental Measurement Approaches

In our consideration of the available experimental methods of measuring D_{12} in supercritical fluid systems, we will concentrate most on one of the more important techniques, but also mention several of the less common methods. This emphasis should not be construed as a judgement of the relative value or merit of each technique. Many of the less common methods produce reliable and valid measurements. They sometimes have limitations in the systems that can be studied. For example, some techniques may be especially adapted for the study of macromolecules. In other instances, there may be inherent restrictions in the temperature and pressure ranges of current instrumentation, a factor that is often overcome as available materials evolve.

Chromatographic Measurement of Diffusion

In the study of supercritical fluid solutions, where high pressures and sometimes high temperatures must be accommodated, the chromatographic method is often the best and sometimes the only applicable technique.[2-8] It is relatively fast, applicable to many solvent-solute systems, and it is certainly the most economical approach among those currently available. For this reason, the chromatographic method will be covered in more detail than the others.

It is interesting to note that the seminal observation that leads to the emergence of the chromatographic measurement of D_{12} actually predates the introduction of gas chromatography by nearly half a century. In 1910, Griffiths[9] performed experiments in which a dye solution was injected into a slowly flowing (i.e., a solution flowing in the laminar regime) stream of solvent in a narrow-bore transparent tube. He noted that the band of color moved along the tube in a well-behaved, symmetrical fashion, but that it slowly increased in width (i.e., it dispersed) during the course of the experiment. These observations were controversial until explained years later by Taylor[10] in 1953 (interestingly, contemporaneously with the development of gas chromatography). Taylor introduced the notion that the dispersion of the dye was due to molecular diffusion along both the axial and radial (parallel to and perpendicular to the tube long axis) directions. In his work, Taylor approximated the relative magnitudes of the axial and radial diffusion. A more general treatment by Aris[11] included them more rigorously.

An idealized representation of the experiment is provided in Fig. 1, in which a uniform, one component fluid is flowing inside of a tube of radius r, and in which the usual parabolic flow profile of the laminar regime prevails. At a time $t = 0$, an additional component (called the solute) is injected into the stream as a pulse resembling a δ-function disturbance in composition. At some later time t, the pulse has broadened, and the disturbance in composition, measured axially at point t by some detection and recording device, now resembles a Gaussian distribution. The inset in Fig. 1 illustrates the idealized measurement of the concentration disturbance.

The similarity of this experiment with open tubular column chromatography (or capillary chromatography) is apparent. While there are a number of possible approaches to the analysis of the flow pattern,[10-13] we will simplify the discussion by presenting only the result, cast in the nomenclature of chromatography.[14] If, for the ideal experiment, we can make the assumptions of 1) a Gaussian solute composition distribution (resulting from an initial δ-function distribution) is obtained; 2) the diffusion tube of Fig. 1 is straight, infinitely long, and of uniform, circular cross section; 3) the fluid velocity is constant, and the flow is laminar; 4) the diffusion coefficient is independent of solute concentration; and 5) the introduction of the solute does not change the fluid density, then

$$H = 2D_{12}/u + r^2u/24D_{12} \tag{2}$$

$$H = \sigma^2 L \tag{3}$$

In these equations, u is the average fluid velocity, assumed to be constant, r is the radius of the tube having length L, and σ^2 is the variance of the Gaussian curve. The quantity H is a common chromatographic parameter. This quantity is measurable from the width of peaks obtained in chromatographic experiments. It is worth noting that although the above result is cast in the language of chromatography, it is obtained with all of the treatments alluded to above. This includes the mathematical models of chromatography that were developed for both chemical analysis and physicochemical measurement applications.[15]

It is important to understand that Eqs. (2) and (3) represent an ideal experiment that cannot be realized in practice. It is only by suitable experimental design, and by the use of appropriate correction factors, that the assumptions stated earlier can be approximated.[16] We will keep the discussion general (i.e., applicable to any chromatographic instrument) by focusing for the moment only on Fig. 1, not on an actual measurement instrument.

A Gaussian distribution of solute concentration is never achieved in a chromatographic experiment because the solute interacts physically with the tube, mainly by adsorption. In addition, the chromatographic experiment is never in a true equilibrium condition. A close approximation to Gaussian behavior can be obtained only if the tube is "inert" to the solute, or can be made such by appropriate chemical treatment. A tube made from high-quality, low-carbon passivated stainless steel such as 316L (ANSI designation) is often suitable for many solutes. Another possibility is silanized fused quartz tubing. Both materials are suitable for operation at elevated pressure and temperature.[17]

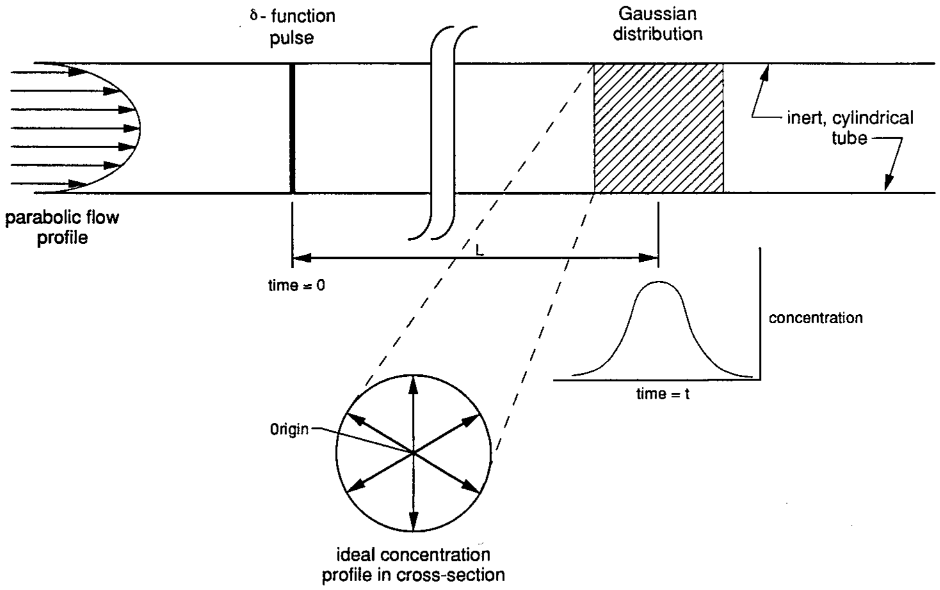

Fig. 1 Idealization of the chromatographic method to measure D_{12}. The inset illustrates the need to determine the solute distribution axially, at a single point.

Injection of the solute as a δ-function spike is not possible in practice, but one can easily provide an approximately rectangular pulse of finite length. The introduction of this pulse will disrupt the flow in the tube. The error associated with this departure from the ideal experiment can be minimized by fast injection, and by using a diffusion tube volume that is large with respect to the volume of the rectangular pulse.

In practice, a straight tube cannot be used since a straight tube of appropriate length cannot be thermostatted on a practical basis. The only practical approach is the use of coiled tubes, which can produce unfavorable secondary flow phenomena. Because of the importance of this in many engineering and physiological processes, a good theoretical framework exists to treat the effect of coiled tubes on the D_{12} measurement. To quantify the effect, we will use, among other quantities, the dimensionless groups mentioned earlier in the introduction:

radius ratio: $\omega = R/r$

Reynolds number: $Re = 2ru\rho/\eta$

Schmidt number: $Sc = \eta/\rho D_{12}$

Dean number: $De = Re\omega^{-1/2}$

If $De^2Sc \leq 20$, one can show that coiling produces an error no larger than 0.05% in the value of D_{12}. This is relatively easy to achieve, because De is dependent on flow rate, a variable that is controllable experimentally.

Nonuniformity in the radius of the diffusion tube is usually insignificant (causing an error of less than 1%) if good quality tubing is used. One must, however, consider the effect of elevated pressure on the actual value of the radius used for calculation.[18] The departure of the diffusion tube cross section from circular is also usually very small. If one considers an elliptical cross section [having semiaxes a_1 and a_2, and an eccentricity $e = 1 - (a_2^2/a_1^2)^{1/2}$] as a limiting case, even an eccentricity of 0.5 produces an error of 0.7% in D_{12}.

The requirement of a constant velocity u is another idealization that is impossible to realize. A pressure gradient must exist in the fluid over L for flow to occur. This must produce a velocity gradient that will be more pronounced at larger values of L. Since having a relatively large tube volume (and therefore, tube length) minimizes flow disruption errors, we must consider this as a tradeoff of experimental parameters, and correct for the most significant error.

Along similar lines, connections of tubing along the length of the diffusion tube must be considered. Such a junction is inevitable, since the tube must be routed to the detector. Since the junction involves a change in radius, the measured D_{12} will change. In addition, the junction is a potential cause of turbulence. It is therefore good practice to minimize the total number of junctions, and to minimize the length of those that are required.

To minimize any concentration dependence of the measured diffusion coefficient, it is important to keep the total amount of injected solute small. A related consideration is that of density disruption. When a solute is injected in the fluid stream, the local density of the fluid clearly changes. This disruption is also minimized by maintaining the solute under infinite dilution conditions, so that the concentration of the diffusing species does not introduce a great departure in density from the solvent. The practical consideration of detectability will govern the amount of solute that must be present in the injected pulse. Some solute-solvent systems are amenable to high sensitivity detection devices, while others are not. Because of this, the error introduced by this departure from the ideal experiment must be determined for each solvent-solute system. If a detector of relatively low sensitivity must be used, the random error incurred may exceed the systematic error introduced by this departure from ideality. Chromatographic detector choice is an involved topic,[14] and cannot be treated adequately in this article.

An additional (subtle but important) implicit assumption in determining (i.e., detecting) the Gaussian-like profile of Fig. 1 is that the profile be determined at a diffusion tube cross section, at a particular axial position. This is illustrated by the inset of Fig. 1. No real detector is capable of such a measurement, because all practical detectors operate from outside the fluid stream, on finite scales of time and displacement, and measurements are performed on finite volumes of solution.

A typical instrument for the determination of D_{12} with the chromatographic method is shown in Fig. 2.[19,20] The fluid to be used as a solvent is supplied either as a liquid or a gas. A high pressure pump, chilled with a vortex tube,[21-24] compresses the fluid to the desired pressure. A forced-air oven contains a heat exchanger (to flash the solvent to the desired supercritical temperature) and the diffusion tube. The 316L stainless steel tube used in this instrument is 34 m in length, with an internal radius of 0.012 cm. A specially designed injector consisting of an extraction pressure vessel and an

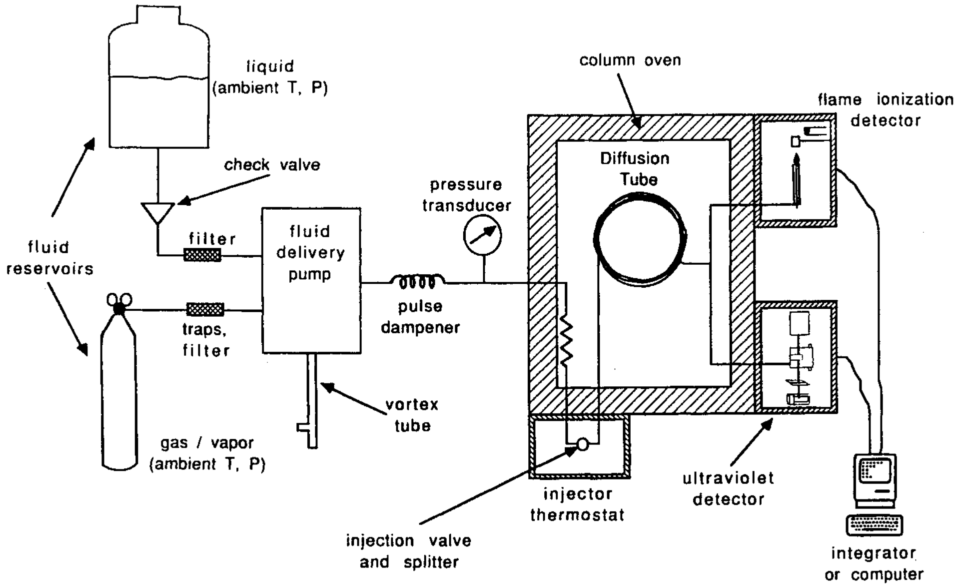

Fig. 2 Practical apparatus for the measurement of D_{12} with the chromatographic method.

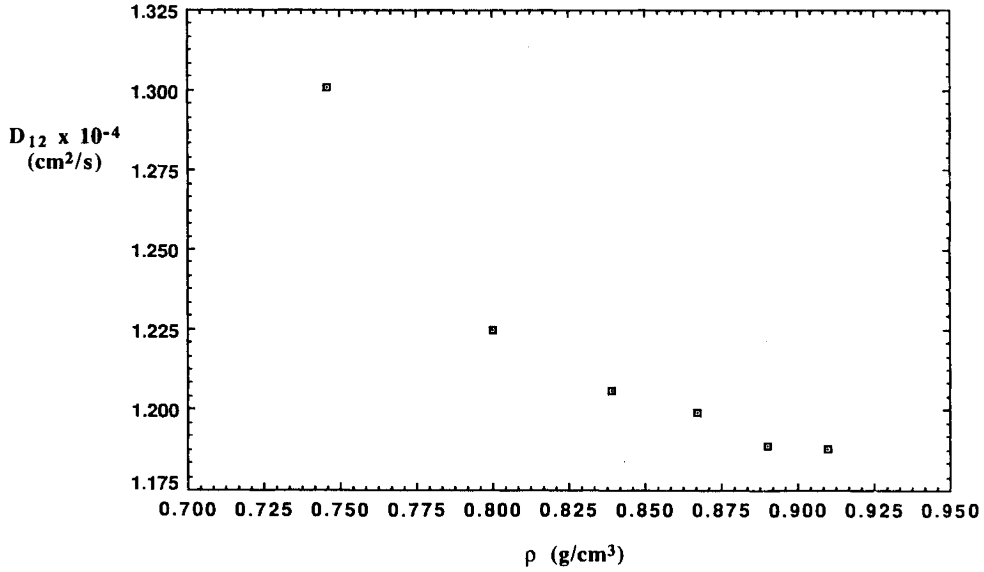

Fig. 3 Diffusion coefficient D_{12}, of toluene in supercritical fluid carbon dioxide solvent, as a function of solvent density.

injection valve[20] is located in a separate oven. A flame ionization detector and a UV-vis spectrophotometer can be used for solute detection. As an example, D_{12} measurements of toluene (as the solute) in supercritical fluid carbon dioxide (as the solvent) are shown in Fig. 3. This is just one of many studies that have been performed with this method.[3–8] Careful attention to the details of experimental design can result in measurements having an accuracy of between 3–5%.

In an interesting extension of this method, Mathews and Akgerman[24] developed a technique for making simultaneously 1) D_{12} measurements on the solvent/solute system, and 2) density measurements on the solvent. Since the solute moves through the diffusion tube at the mean velocity of the carrier solvent, the c.g. (or normalized first moment) of the detected peak can be related to the mass flow rate of the carrier fluid. In simple terms, the mass flow rate is the product of fluid velocity, density, and cross-sectional area of the diffusion tube. The mass flow rate of a reference fluid (of known density under the temperature and pressure of interest) is determined with a tracer solute (at infinite dilution). The unknown density of another fluid is then determined by computing the volume ratio of the fluid of known density with that of unknown density. This method is applicable when the density and relative molecular mass of the solvent and solute are similar, a situation that can arise in thermally stressed turbine fuels.

Measurement of D_{12} by Light Scattering

When a beam of monochromatic light passes through a fluid (even a simple fluid), some of the light is scattered by the molecules. The light interacts with the electrons on a molecule. Because the molecules are in a constant state of motion, local heterogeneities or fluctuations are created in the medium. If the medium is a dielectric, a change in the dielectric susceptibility (and therefore, refractive index) of the fluid will be associated with these fluctuations. The majority of the scattered light is centered in a band at the same frequency as the incident beam, and is called Rayleigh scattering. The width (at half-height) of this scattered band is related to the Brownian motion of the molecules.

In a binary mixture, Brownian motion fluctuations are caused by both temperature and compositional inhomogeneity, and both contribute to the linewidth. The thermal fluctuations result in thermal diffusivity χ, and the compositional fluctuations result in the effect represented by D_{12}. When the time scales and magnitudes of these fluctuations are sufficiently different (i.e., $\chi >> D_{12}$, or $\chi << D_{12}$), the temperature and compositional contributions can be decoupled and measured separately.

The actual measurement technique used is quasielastic light scattering or photon correlation spectroscopy. The measured quantity is the field autocorrelation function, from which D_{12} can be determined upon suitable normalization and curve fitting.[25,26]

While light scattering is attractive, there are practical limitations in temperature and pressure ranges. In addition, the best results are obtained when the solute molecule is quasispherical and large, and the solution is relatively concentrated. When the method is applicable, however, it is probably the most accurate method, having typical experimental uncertainties in the range of 0.5%. A major practical disadvantage of the technique is that the cost of the instrumentation is very high.

Nuclear Magnetic Resonance (NMR) Spectroscopic Method

Nuclear magnetic resonance spectrometry can be used to measure D_{aa}. It is mentioned in the context of this review only because it has been used to measure self diffusion of a solute in supercritical fluid solutions. While a discussion of Fourier transform NMR is beyond the scope of this review, a recently developed technique using this method is worthy of mention.[27] If a molecule has two magnetically different nuclei, the application of a magnetic field will allow the observation of different absorptions, called chemical shifts. A pulse of radio-frequency energy normal to the magnetic field will separate (dephase) the spin vectors corresponding to these nuclei. After some time τ, an additional pulse, applied 180 deg to the field, will cause the vectors to rephase. When the vectors are again in phase, a measurable echo will be produced. The experiment is therefore called a $90 - \tau - 180$ spin echo measurement. The amplitude of the echo maximum, which can be fit to a Bessel function, contains the diffusion coefficient in an exponential term. This technique appears capable of operation at very high pressures, although the temperature range may be limited. It is also limited to relatively simple solute-solvent systems, and, as with light scattering, involves complex and very expensive instrumentation.

Physical Methods

We will complete our discussion of measurement techniques by mentioning an interesting physical method that can be used with a solid solute if the solubility of the solute in the supercritical fluid solvent is known. A glass capillary is partly filled with the solute, and is placed in a concentric holder inside a pressure vessel. The vessel is then flooded with the solvent under the desired supercritical fluid temperature and pressure. The solute will enter solution, and produce an "evaporation front" in the capillary. A measurement of the size of this evaporation front, the solid solute density, the solute solubility, and the elapsed time of the experiment can be used to calculate D_{12}.[28]

Although this and similar methods have the potential of application under relatively high temperature and pressure, there are many significant limitations. The duration of an experiment is very long, approaching 40 h, and relevant solubility data is scarce. In addition, the method has a relatively low precision.

Conclusions

In this article, we have reviewed the more important experimental measurement methods available for the measurement of binary interaction diffusion coefficients in supercritical fluid solutions. The chromatographic method, which is the most generally applicable and economical, requires attention to the departures from the ideal experiment. These departures must be addressed by careful experimental design, or by the application of suitable correction factors. The other techniques described, namely light scattering, NMR, and physical methods, have more limited application to specific situations.

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