

DIFFUSION COEFFICIENT MEASUREMENTS USING STEFAN TUBE AT SUPERCRITICAL CONDITIONS

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Applicability of Stefan tube at the supercritical conditions for the diffusion coefficient measurements of a system of a solid solute and a supercritical fluid is evaluated. The prototype used to evaluate the approach is naphthalene-supercritical carbon dioxide. An initial theoretical calculation with available data, show that, the diffusion process would be in the unsteady state region for a practical duration of experiment. The development of a theoretical model was carried out for systems where the transport of the species is dominated only by diffusion as well as for systems involving convective transport along with diffusion for finite as opposed to a semi-unbounded control volume. The binary diffusion coefficients were determined at 35, 50 and 65 °C for the pressures, 80, 100 and 120 atm. The quantification of the convective term showed little effect on the diffusion coefficient for the supercritical naphthalene-carbon dioxide system. The concentration curves were redrawn with the evaluated data confirming the unsteady state. The evaluated diffusion coefficients are in good agreement within each other and with literature therefore validate Stefan tube's applicability for diffusion coefficient measurements at supercritical conditions.

INTRODUCTION

Over the last three decades, supercritical processes and supercritical solvents, particularly supercritical carbon dioxide has gained wider use and more interest [1]. Therefore, for the design and operation of such processes, the availability of reliable transport properties for different chemical systems and for relevant conditions of operation is vital. However, the currently available correlations and predictions vary greatly among themselves and are system dependent [2]. There are a number of experimental techniques developed for the measurement of the diffusion coefficients at supercritical conditions. Liang et al.[3] in their review paper discussed the shortcomings and advantages of the existing experimental techniques.

The Stefan tube, originally developed from J. Stefan's work in 1889 [4], was adapted and used for diffusion coefficient measurements by Arnold [5], and Slattery and Mhetar [6] at ambient conditions. The significance of the Stefan tube arises from the basics of diffusion in the Stefan tube being closely related to several research areas like drying of porous materials and considerations on the meso- and macro- pore level transport, which are very often formulated in terms of fluxes and driving forces for the transfer of the species [7]. The system may be considered either steady state or unsteady state depending on the properties of the diffusing species, the medium of diffusion and the duration of the experiments. The experimental parameter to be measured is concentration or mass changes in order to calculate the diffusion coefficient from the governing relationships of a material balance for a solute for an infinitesimal

element within the solvent phase. The resulting equation to be solved is effectively a one dimensional mass-transfer problem coupled with the boundary conditions. In this paper, we explore the applicability of the Stefan tube in the diffusion coefficient measurements of non-volatile solids in supercritical fluids. The carbon dioxide-naphthalene system is used as the model system. The diffusion process has been analyzed in the presence of possible convective forces contributing to the transport of species to investigate their effect.

THEORETICAL BACKGROUND

The representation of the diffusion medium studied is one, where solid naphthalene at the bottom of the tube is evaporating into the supercritical carbon dioxide that fills the rest of the tube and is carried away by the pure supercritical carbon dioxide that is flowing from the top of the tube (Figure 1). The diffusion medium is bounded by the $z=0$ and the $z=h$ planes, where the $z=0$ plane starts above a thin film region where the supercritical carbon dioxide is saturated with solid naphthalene. The system is maintained in a temperature-controlled and pressure regulated medium to ensure isothermal and isobaric operation throughout.

Since the diffusion is only in the z -direction, the equation of continuity reduces to,

$$\frac{\partial y_A}{\partial t} + \hat{v}_z^* \frac{\partial y_A}{\partial z} = D_{AB} \frac{\partial^2 y_A}{\partial z^2} \quad (1)$$

where the initial and boundary conditions are,

$$\left. \begin{array}{lll} \text{IC} & t=0 & y_A = y_{A_i} = 0 \\ \text{BC1} & z=0 & y_A = y_{A_0} = y_A^{\text{eq}} \\ \text{BC2} & z=h & y_A = y_{A_h} = 0 \end{array} \right\} \begin{array}{l} \text{for } 0 < z < h \\ \text{for } t > 0 \end{array}$$

In equation (1), the term \hat{v}_z^* , needs to be defined and inserted in the equation, to be able to proceed with the solution. Assuming that is constant for cases with convection or zero for cases without convection, one can proceed with following dimensionless representation and solutions.

Introducing the dimensionless variables

$$\theta = \frac{y_A}{y_{A_0}}, \quad \eta = \frac{z}{h}, \quad \tau = \frac{D_{AB}t}{h^2}$$

into equation (1), the following equation is obtained,

$$\frac{\partial \theta}{\partial \tau} + B \frac{\partial \theta}{\partial \eta} = \frac{\partial^2 \theta}{\partial \eta^2} \quad (2)$$

where $B = \frac{\hat{v}_z^* h}{D_{AB}}$ is the dimensionless convective term. The general form of the solution will be,

$$\theta(\eta, \tau) = \theta_{\infty}(\eta) - \theta_t(\eta, \tau) \quad (3)$$

where $\theta_{\infty}(\eta)$ is the steady state part of the solution and $\theta_t(\eta, \tau)$ is the transient part of the solution, which fades out as time goes to infinity. The steady state and the transient parts of this general solution are solved separately and then combined for the final solution. Substituting the transient solution and the steady state solution into equation (3), the general solution that includes significant amount of convection will be obtained,

$$\theta(\eta, \tau) = \frac{\exp(B\eta) - \exp(B)}{1 - \exp(B)} - \sum_{n=1}^{\infty} \frac{8n\pi}{B^2 + 4n^2\pi^2} \exp\left[(-n^2\pi^2 + \frac{B^2}{4})\tau + \frac{B}{2}\eta\right] \sin n\pi\eta \quad (4)$$

Then, starting with rate of mass loss of solute from surface area S,

$$\frac{\partial M}{\partial t} = S(MW)N_{A_{z=0}} \quad (5)$$

where M is the amount of evaporated naphthalene at time t, and MW, is the molecular weight of naphthalene and the flux of naphthalene at the surface of the solid phase to be

$$N_{A_{z=0}} = -\frac{cD_{AB}}{1 - y_{A_0}} \frac{\partial y_A}{\partial z} \Big|_{z=0} \quad (6)$$

one can obtain the final mass loss equation as for instances with convection

$$M_f = \frac{Sh(MW)cy_{A_0}}{1 - y_{A_0}} \left(\frac{D_{AB}t_f}{h^2} \cdot \frac{B}{(e^B - 1)} + \sum_{n=1}^{\infty} 32\pi^2 n^2 \left[\frac{1 - \exp\left[\left(-n^2\pi^2 + \frac{B^2}{4}\right)\frac{D_{AB}t_f}{h^2}\right]}{16n^4\pi^4 - B^4} \right] \right) \quad (7)$$

and the following for which B is zero

$$M_f = Sh(MW)c \frac{y_{A_0}}{1 - y_{A_0}} \left[\frac{D_{AB}t_f}{h^2} + 2 \sum_{n=1}^{\infty} \frac{1 - \exp\left[-n^2\pi^2 \frac{D_{AB}t_f}{h^2}\right]}{n^2\pi^2} \right] \quad (8)$$

EXPERIMENTAL

The detail of the experimental system is given elsewhere [8]. The diffusion tube is a ¼” O.D. and 1/8” I.D. stainless steel tube, which is capped at one end and open at the other to be connected to the gas line of stainless steel tubing, for the supercritical carbon dioxide to flow above the tube entrance. The total length of the diffusion tube was 11.5 cm and the diffusion medium was 9.6 cm, with the naphthalene loaded. A medium pressure digital density meter (Model: DMA60, Anton Paar GmbH, Austria), with a remote measuring cell (Model: DMA512), for flow type measurements, is used for the monitoring of the density of the system.

The experiments lasted for 15 hours of continued flow of carbon dioxide, pressurized and fed by the syringe pump, over the Stefan tube that contains pre-weighed amount of naphthalene. The steady state is achieved only after about 50 hours and, therefore, the primary consideration for the experimental time determination is the accuracy of the gravimetric considerations. The entire system was at constant temperature and pressure. At the end of the experiment, the amount of naphthalene was determined gravimetrically.

RESULTS

Table 1 exhibits the data collected from the experimental runs at 35, 50 and 65 °C for 80, 100 and 120 atmospheres and the results for these conditions. The third column shows the solid naphthalene mass loss, evaluated by weighing the tube filled partially with compressed naphthalene, before and after the experiments, which were run twice. The fourth column is the density of the naphthalene supercritical carbon dioxide mixture measured by the density meter described in the Experimental Section. The evaluated equilibrium solubility mole fractions of naphthalene in supercritical carbon dioxide are given in the fifth column and are computed from SRK equation of state with regressed interaction coefficient. The sixth column is the molar density of the naphthalene supercritical carbon dioxide mixture, converted from the values listed in column four. These are the data required for the evaluation of the diffusion coefficients. The subsequent columns show the results from the procedure with and without convection.

CONCLUSIONS

An analysis of the Stefan tube at supercritical conditions for the diffusion coefficient measurements has been carried out. The binary diffusion coefficients for the system naphthalene-supercritical carbon dioxide were determined at 35, 50 and 65 °C for the pressures, 80, 100 and 120 atmospheres. The models developed both for systems with convection and for systems without convection were employed to quantify and compare the convective effect on the diffusion coefficients. Results showed no significant effect of convection on the diffusion coefficients for naphthalene-supercritical carbon dioxide system. The concentration profiles drawn with the measured data confirmed the initial determinations of the unsteady state of the diffusion process. The determined diffusion coefficients agree well with literature and confirm the behavior of a supercritical diffusion coefficient under the influence of temperature and pressure changes which result in density changes of the supercritical solvent.

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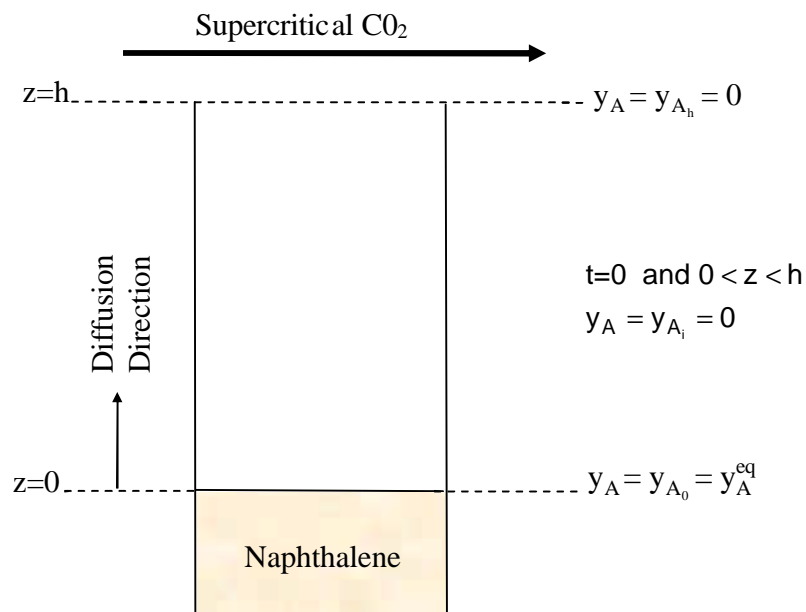


Figure 1. Schematic of Stefan Tube for the Study of the Diffusion of Naphthalene in Supercritical Carbon Dioxide

Table 1. Collected data and the calculated D_{AB} values for convection and non-convection systems

Temperature, °C	Pressure, atm	Evaporated naphthalene ⁽¹⁾ , mg	Measured density ⁽²⁾ , g/cm ³	Mole fraction of naphthalene solubility ⁽³⁾	Molar density ⁽⁴⁾ , gmol/cm ³	Convection included (B ⁽⁵⁾ ≠0, v _z ≠0)			No Convection (B=v _z =0)
						B×10 ³	v _z ×10 ⁷ [cm/s]	D _{AB} ×10 ⁴ [cm ² /s]	D _{AB} ×10 ⁴ [cm ² /s]
35	80	2.2	0.4648	0.004986	0.010461	14.710	3.840	2.505	2.510
		2.1	0.4650	0.004986	0.010466	15.409	3.662	2.281	2.286
35	100	4.4	0.7272	0.008135	0.016270	30.529	4.935	1.552	1.554
		4.3	0.7268	0.008135	0.016261	31.220	4.826	1.484	1.486
35	120	5.1	0.7792	0.010650	0.017352	48.242	5.364	1.067	1.068
		5.1	0.7800	0.010650	0.017369	48.289	5.359	1.065	1.066
50	80	0.4	0.2269	0.001226	0.005144	2.449	1.419	5.562	5.581
		0.4	0.2254	0.001226	0.005110	2.436	1.429	5.631	5.650
50	100	2.1	0.4098	0.004869	0.009226	12.974	4.154	3.074	3.079
		2.1	0.4097	0.004869	0.009223	12.971	4.155	3.075	3.081
50	120	5.3	0.5995	0.010435	0.013355	34.323	7.242	2.025	2.021
		5.2	0.5988	0.010435	0.013340	34.941	7.114	1.954	1.950
65	80	0.4	0.1850	0.001347	0.004192	2.463	1.741	6.786	6.804
		0.4	0.1856	0.001347	0.004206	2.469	1.735	6.747	6.766
65	100	1.0	0.2752	0.002838	0.006219	6.277	2.934	4.487	4.505
		1.0	0.2752	0.002838	0.006219	6.277	2.934	4.487	4.505
65	120	2.4	0.3953	0.007285	0.008859	24.424	4.944	1.943	1.945
		2.5	0.3951	0.007285	0.008854	24.412	4.947	1.945	1.947

⁽¹⁾ For each temperature and pressure combination, two experiments were conducted

⁽²⁾ The measured density of the binary mixture, C_g .

⁽³⁾ The solubility mole fraction of naphthalene was calculated using the SRK EOS to fit literature data

⁽⁴⁾ Molar density of binary mixture was calculated by using the relation, $C=C_g/MW_s$ where MW_s is the molecular weight of the solution and is calculated by: $MW_s = y_{A0} * MW_N + (1-y_{A0}) * MW_{CO2}$ where MW_N , molecular weight of naphthalene, MW_{CO2} , molecular weight of CO₂, and y_{A0} , the equilibrium solubility molar fraction of naphthalene.

⁽⁵⁾ Dimensionless convective term ($h \cdot v_z / D_{AB}$), where h is the height of the stagnant gas layer, v_z is the average molar velocity and D_{AB} is the diffusion coefficient.