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Molecular Diffusion Coefficients and Effective Diffusivities of 1-Octene in Supercritical Ethane in Relation to Fischer−Tropsch Synthesis

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Fischer−Tropsch synthesis employing supercritical fluid reaction media offers mass transfer advantages over conventional processes. Data are needed to calculate effective diffusivities in catalyst pores, for which molecular diffusion coefficients in the supercritical media as well as the catalyst porosity and tortuosity are required. The Taylor dispersion technique was used to measure the molecular diffusion coefficients. A tracer response technique was used to measure the effective diffusivities employing 1-octene in supercritical ethane (P_c = 48.8 bar, T_c = 305.4 K) as the model system with an iron-based Fischer−Tropsch catalyst. Measurements were made in the temperature range of 523−543 K and pressure range of 62−144 bar. The results were analyzed by the subtraction of moments method. The precision of the results is within approximately 15%. The average value of tortuosity divided by particle porosity (τ/ϵ_p) is (9.72 ± 1.22), while the average value of τ is (6.10 ± 0.766) using the particle porosity set at 0.628.

Introduction

In Fischer−Tropsch synthesis (FTS), liquid hydrocarbons are formed from synthesis gas employing, most frequently, an iron-based catalyst. Recently we conducted a study of FTS in supercritical propane as a model system (Lang *et al.*, 1995). In order to model the reaction data, effective diffusivities ($D_{\rm eff}$) in the catalyst pores are needed. The effective diffusivities are related to the molecular diffusion coefficients. Using the relationship

$$D_{\rm eff} = (\epsilon_p/\tau)/D_{12} \qquad (1)$$

if the tortuosity τ and particle porosity ϵ_p were known, only the molecular diffusion coefficient D_{12} would need to be determined by experiment. Unfortunately, there are few studies at these conditions, and the tortuosity and porosity of each catalyst particle must be determined independently. On the other hand, if ϵ_p/τ is determined at one set of conditions, $D_{\rm eff}$ can then be calculated at any other set of conditions provided that D_{12} is known or can be estimated.

Effective diffusivities were measured for an iron-based FTS catalyst, Ruhrchemie LP 33/81, in a 1-octene−supercritical ethane system at 523, 533, and 543 K in the pressure range of 62−144 bar using a tracer response technique with the subtraction of moments method. The axial dispersion coefficients, adsorption equilibrium constants, and molecular diffusion coefficients were also measured at each set of experimental conditions.

Experimental Procedure

A diagram of the experimental apparatus is shown in Figure 1, which is similar to that used by Erkey and Akgerman (1990). The syringe pump, ISCO LC-2600, is filled with liquid solvent and pressurized in a closed environment to the desired operating conditions. Ethane is allowed to flow through stainless steel tubing to a preheater in the furnace. The furnace is heated and is accurate within 1 °C. The supercritical fluid then passes through an injection valve to a stainless steel column with an approximate diameter of 0.635 cm packed with Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on mass basis) or through a 15.84 m long Taylor dispersion coil, or through a bypass line. This switching between the apparatus was completed by two zero dead volume connections that could be unconnected and reconnected without added dispersion. The bypass was employed to measure the amount of dispersion incurred in the system (minus the packed column or the dispersion coil) due to flow and most important due to the cooling length necessary, since the detector cannot handle the high-temperature fluid. An accurate measure of the internal volume of the column was determined by a method of weighing the column filled with distilled and deionized water as described by Erkey and Akgerman (1990). After the column or the dispersion coil, the supercritical fluid passes to a high-pressure UV detector (ISCO V^4) with a dead volume of 0.25 μL. The system pressure is set by a back-pressure regulator (Tescom 26-1722-24) placed after the UV detector. A second back-pressure regulator (Grove SD91-W) at 54.4366 atm reduced pulsations in the system by utilizing a double expansion technique (Erkey and Akgerman, 1990). The system pressure was measured by an internal pressure transducer in the syringe pump calibrated to a precision of ±1 bar.

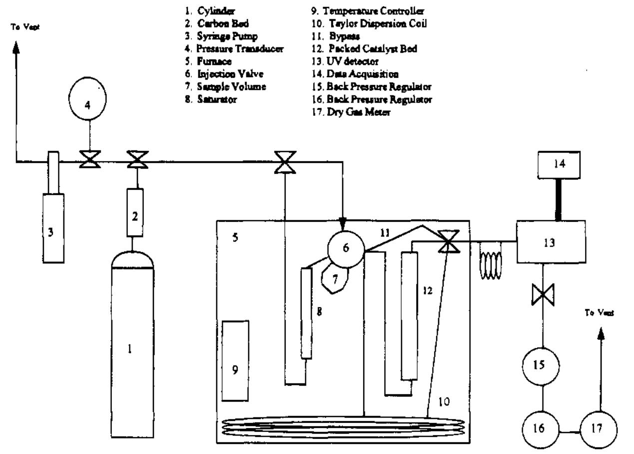

Figure 1. Experimental setup for the determination of the effective diffusivities and molecular diffusion coefficients.

The Taylor dispersion tubing was coiled to a diameter of 0.28 m to allow it to fit into the furnace. The maximum flow rate that can be used in the diffusion coil depends on many criteria which are summarized by Erkey and Akger-

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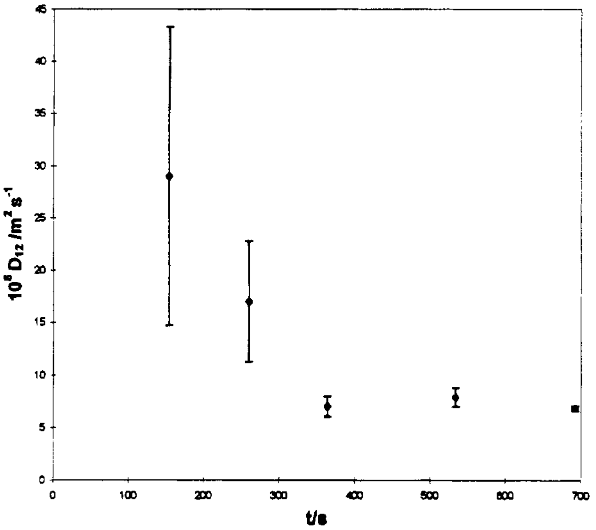

Figure 2. Effect of the flow rate on the diffusion coefficient measured (increased residence time *t* implies lower flow rate).

Table 1. Properties of the Packed Catalyst Bed

bed length	0.254 m
bed diameter	0.003 175 m
bed porosity	0.359
particle radius	0.000 245 m
particle porosity	0.628
particle density	1050 kg/m^3
specific surface area	295 m^2/g

man (1991), and flow rates of less than 9 mL/h were used. The effect of flow rate (range of 5–20 mL/h) on the molecular diffusion coefficient extracted from Taylor dispersion data is illustrated in Figure 2. At the same conditions as the flow rate is increased the residence time is decreased. As shown, if the flow rate is above the criteria's maximum, then results will scatter mostly because of secondary flow effects (Erkey and Akgerman, 1991). A set of six experiments were completed at each temperature and pressure condition for both the Taylor dispersion coil and the bypass in order to obtain an accurate measurement of the molecular diffusion coefficients and to confirm the reproducibility of the experiments.

Flow rates of the solvent varied from 25 to 100 mL/h with an accuracy of ±4% for effective diffusivity measurements. The injection valve contains a 10 μL sample of solute dissolved in supercritical fluid. This sample is produced by injection of 3 mL of solute into a saturation system, with a volume of 9 mL, placed before the injection valve. Supercritical fluid is then put into the saturator and left for sufficient time to dissolve the solute injected. A column frit is placed before the saturator to reduce entrainment of the solute fluid. The 10 μL sample is injected into the column, which is filled with catalyst, and the response is measured on-line with the UV detector and recorded in 1 s intervals by means of an Intel 486 SX computer. This procedure was completed three times at each flow rate, pressure, and temperature condition to obtain an accurate result.

The catalyst was prepared by crushing and sieving particles to a size of approximately 250–295 μm. The catalyst was then calcined at a temperature of 673.15 K for a period of 4 h and resieved to eliminate any particles which were reduced in size during the calcining process. The properties of the particles are given in Table 1. The particle porosity as well as the mean pore size and the specific surface area was determined by standard nitrogen adsorption techniques, completed independently. The particle density was determined by pycnometer analysis. The bed porosity was determined from the mass of a known volume of particles.

Results and Discussion

The mass transfer in a catalyst bed is governed by a set of three partial differential equations (Wakao and Kaguei, 1982). In these equations the film mass transfer coefficient k_f and the axial dispersion coefficient D_{ax} are system dependent parameters (column dimensions, packing type, hydrodynamics) whereas the effective diffusivity D_{eff}, the adsorption equilibrium constant K_A, and the adsorption rate constant k_a are intrinsic parameters for a given catalyst. From these equations the effective diffusivity and axial dispersion coefficient of the packed bed column may be obtained from the first and second moments (residence time and variance) of the peak. The equations for the mean residence time and variance of the tracer response are (Wakao and Kaguei, 1982)

$$t_r = \mu_1 - \mu_I = (L_t/U)(1 + \delta_0) \tag{2}$$

$$\sigma_m^2 = \mu_2 - \mu_{II} = \frac{2L_t}{U}\left[\delta_1 + D_{ax}(1 + \delta_0)^2\frac{1}{U^2}\right] \tag{3}$$

where

$$\delta_0 = \frac{1 - \epsilon_b}{\epsilon_b}[\epsilon_p + \varrho_p K_A] \tag{4}$$

$$\delta_1 = \frac{1 - \epsilon_b}{\epsilon_b}\left[\frac{\varrho_p K_A^2}{k_a} + (\epsilon_p + \varrho_p K_A)^2\left(\frac{1}{5D_{eff}} + \frac{1}{k_f R_t}\right)\frac{R_t^2}{3}\right] \tag{5}$$

In the above equations, L_t is the length of the column, U is the interstitial velocity, ϵ_b is the catalyst bed porosity, ρ_p is the bulk catalyst particle density, and R_t is the column radius. The variables μ_1 and μ_2 are the first and second moments, respectively, due to the experiments completed with the packed bed of catalyst, whereas μ_I and μ_{II} are the moments with the packed column removed from the system, i.e., moments obtained by flowing through the bypass line. Normally a real time domain fitting of these equations would yield the parameters, but there is a very large change in density (hence the residence time and variance) due to cooling from measurement temperatures to room temperature before the detector. The subtraction of moments procedure eliminates any extra dispersion caused by the cooling coil, as well as the UV detector dead volume, the injection valve, and any nonzero dead volume connections. The first and second moments are calculated from the experimental data using the following equations:

$$\mu_1 = \frac{\sum_{i=1}^{n-1}(t_i + t_{i+1})(C_i + C_{i+1})}{2\sum_{i=1}^{n-1}(C_i + C_{i+1})} \tag{6}$$

$$\mu_2 = \frac{\sum_{i=1}^{n-1}(t_i + t_{i+1})^2(C_i + C_{i+1})}{4\sum_{i=1}^{n-1}(C_i + C_{i+1})} - \mu_1^2 \tag{7}$$

where t is the time at a given point, C is the concentration at a given point, and n is the total number of points. The calculation of the functions μ_I and μ_{II} is completed in the same manner.

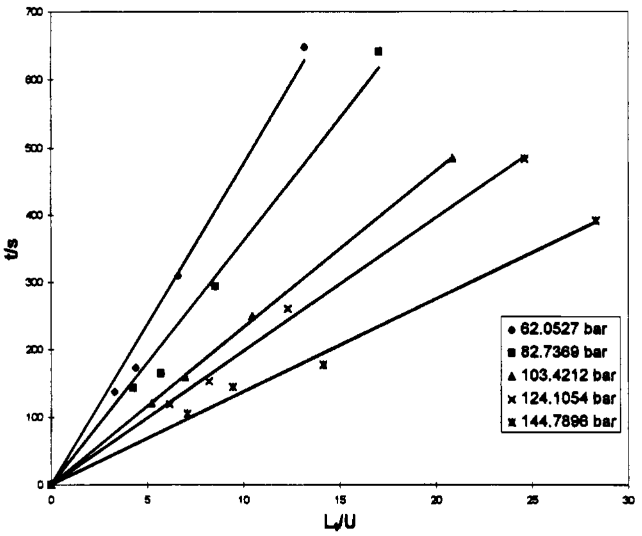

Figure 3. Variation of the residence time t with L_t/U at 523 K.

Table 2. Adsorption Equilibrium Constants for 1-Octene–Ethane

T/K	P/bar	ρ/(kg m^{-3})	10^3K_A/m^3 kg^{-1})
523	62.0527	45.69	23.821
523	82.7369	61.92	18.146
523	103.4212	78.39	14.25
523	124.1054	94.88	9.437
523	144.7896	111.16	6.209
533	62.0527	44.6	17.419
533	82.7369	60.337	15.480
533	103.4212	76.26	12.806
533	124.1054	92.186	7.785
533	144.7896	107.906	6.136
543	62.0527	43.57	15.447
543	82.7369	58.848	14.620
543	103.4212	74.28	12.378

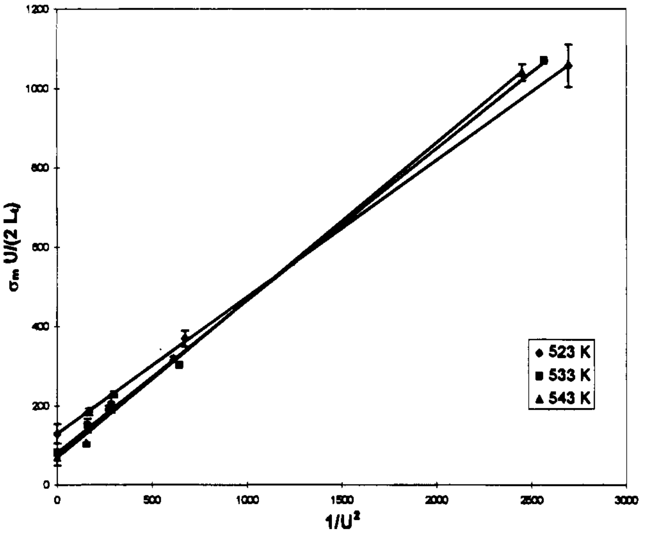

Figure 4. Determination of effective diffusivities: variation of $(\sigma U)/(2L)$ with $1/U^2$ at 62.053 bar.

Table 3. Effective Diffusivity and Peclet Number

T/K	P/bar	ρ/(kg m^{-3})	10^8D_{eff}/(m^{2}s^{-1})	$Pe(Ud_pD_{ax}{}^{-1})$
523	62.0527	45.69	0.923 ± 0.200	0.030319
523	82.7369	61.92	0.650 ± 0.175	0.025529
523	103.4212	78.39	0.498 ± 0.100	0.022887
523	124.1054	94.88	0.426 ± 0.210	0.020294
523	144.7896	111.16	0.408 ± 0.132	0.013978
533	62.0527	44.6	0.803 ± 0.140	0.01542
533	82.7369	60.337	0.610 ± 0.152	0.016851
533	103.4212	76.26	0.488 ± 0.200	0.018554
533	124.1054	92.186	0.590 ± 0.276	0.013077
533	144.7896	107.906	0.493 ± 0.205	0.022794
543	62.0527	43.57	0.742 ± 0.175	0.012177
543	82.7369	58.848	0.520 ± 0.154	0.018833
543	103.4212	74.28	0.692 ± 0.212	0.020553

The adsorption equilibrium constant is the only parameter in the first moment equation which is unknown. From the slope of a plot of the residence time versus L_t/U the adsorption equilibrium constant can be determined. Figure 3 is a representative plot. The adsorption equilibrium constant can be determined from the slope of the line. The results are given in Table 2.

The second moment (eq 3) involves four additional parameters that must be determined. In order to extract the effective diffusivity, some assumptions are made. First, it was estimated that the external mass transfer coefficient was much larger than the effective diffusivity in this study. Thus, the term $1/(k_fR_t)$ in eq 5 is much smaller than $1/(5D_{\text{eff}})$ and can be neglected. This is based on calculations using a correlation by Lim et al. (1989) for mass transfer coefficients. A second simplification was to neglect the contribution of the rate of physical adsorption to peak dispersion. Adsorption rates are typically very fast (Wakao and Kaguei, 1982), i.e., $k_a \rightarrow \infty$, and the contribution of the first term in eq 5 becomes negligible. With these simplifications eq 3 reduces to

$$\sigma_m^{\ 2} = \frac{2L_t}{U}\left[\frac{1-\epsilon_b}{\epsilon_b}\left[(\epsilon_p + \varrho_p K_A)^2\left(\frac{R_t^{\ 2}}{15D_{\text{eff}}}\right)\right] + (1+\delta_0)^2\frac{D_{ax}}{U^2}\right] \tag{8}$$

If the axial dispersion coefficient is assumed to be constant over the range of Reynolds numbers studied (Bischoff, 1960), then a plot of $(\sigma_m{}^2U)/(2L_t)$ with respect to $1/U^2$ should be linear and the catalyst effective diffusivity and the bed axial dispersion coefficient can be determined from the intercept and the slope, respectively. Figure 4 gives a representative plot, and the values of the effective diffusivities and the Peclet number Ud_p/D_{ax} are summarized in Table 3. The Peclet numbers are reported although they are not important since they are system dependent hydrodynamic parameters.

Unlike the effective diffusivity technique, the Taylor dispersion technique is governed by a single partial differential equation. Using the continuity equation as outlined by Taylor (1953), Hunt (1976), and Aris (1956), an equation for the diffusion coefficient can be derived. The molecular diffusion coefficient was obtained using the method of moments as described in Alizadeh *et al.* (1980) and Matthews (1988), using results of Aris (1956), Levenspiel and Smith (1957), and Pratt and Wakeham (1975). In this methodology, the first and second moments of the peak are used to calculate the diffusion coefficient. The equation for the mean residence time and variance is (Pratt and Wakeham, 1975)

$$t_{r_{id}} = t_{r_{obs}} - t_{r_i} \tag{9}$$

where $t_{r_{id}}$ = corrected residence time, $t_{r_{obs}}$ = first moment of the response signal with the diffusion tube, and t_{r_i} = first moment of the input signal without the diffusion tube. Similarly,

$$\sigma_{id}^{\ 2} = \sigma_{obs}^{\ 2} - \sigma_i^{\ 2} \tag{10}$$

where σ_{id} = corrected variance, σ_{obs} = second moment of the response signal with the diffusion tube, and σ_i = second moment of the input signal without the diffusion tube. Knowing the corrected moments allows one to calculate the

Table 4. Molecular Diffusion Coefficients and D_{12}/D_{eff}

T/K	P/bar	ρ/(kg m^{-3})	$10^8 D_{12}$/m^2 s^{-1}	D_{12}/D_{eff}	τ
523	62.0527	45.69	7.03 ± 0.246	7.62	4.79
523	82.7369	61.92	6.10 ± 0.99	9.38	5.89
523	103.4212	78.39	4.99 ± 0.606	10.01	6.29
523	124.1054	94.88	4.49 ± 0.524	10.56	6.63
523	144.7896	111.16	4.37 ± 0.139	10.95	6.88
533	62.0527	44.6	6.91 ± 0.240	8.60	5.40
533	82.7369	60.337	5.90 ± 0.66	9.66	6.07
533	103.4212	76.26	5.71 ± 0.668	11.70	7.35
533	124.1054	92.186	5.27 ± 0.0676	8.13	5.10
533	144.7896	107.906	5.45 ± 0.0779	10.77	6.76
543	62.0527	43.57	6.70 ± 0.278	9.03	5.67
543	82.7369	58.848	6.00 ± 0.45	10.89	6.84
543	103.4214	74.28	6.29 ± 0.734	9.09	5.71
			av:	9.72 ± 1.22	6.10 ± 0.766

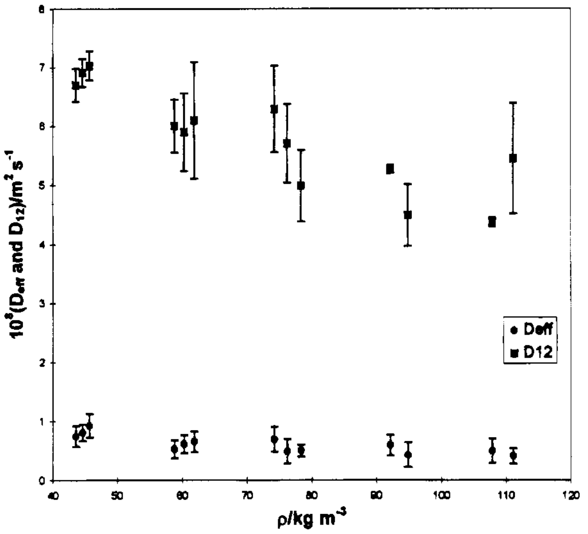

Figure 5. Density dependency of the molecular diffusion coefficient and the effective diffusivity.

molecular diffusion coefficient from the equation (Matthews, 1988)

$$D_{12} = \frac{1}{2}\left(\frac{L^2}{t_{id}}(1 + 2\zeta_0)\zeta_0 - \left[\frac{L^4}{t_{id}^2}\zeta_0^2(1 + \zeta_0^2) - \frac{4L^2R^2}{48t_{id}^2(1 + 2\zeta_0)^2}\right]^{1/2}\right) \quad (11)$$

where

$$\zeta_0 = \frac{2\sigma_{id}^2 - t_{id}^2 + [t_{id}^4 + 4t_{id}^2\sigma_{id}^2]^{1/2}}{[8t_{id}^2 - 4\sigma_{id}^2]} \quad (12)$$

In the above equations, L is the length of Taylor dispersion tubing and R is the inner radius of the tube. Thus, by inserting eqs 9, 10, and 12 into eq 11, the molecular diffusion coefficient can be determined. According to Alizadeh *et al.* (1980), these results are accurate to approximately 1%, providing that the design criteria are met.

Results for molecular diffusion coefficients and the D_{12}/D_{eff} ratio for the 1-octene–ethane system are presented in Table 4. The variation of the diffusion coefficient and the effective diffusivity with respect to the solvent density is displayed in Figure 5. As the density of the fluid increases, both the molecular diffusivity and the effective diffusivity decrease. The ratio of the molecular diffusion coefficient to the effective diffusivity, D_{12}/D_{eff}, should be a constant equal to τ/ϵ_p (Erkey and Akgerman, 1990). Figures 6 and 7 show that D_{12}/D_{eff} and τ are nearly constant which is also indicative of consistency of experimental measurements and data reduction procedures. The D_{12}/D_{eff} ratio in Table 4 specifies a tortuosity value of (6.10 ± 0.766) which is reasonable since tortuosity factors reported for other catalysts are in the range of approximately 2–8.

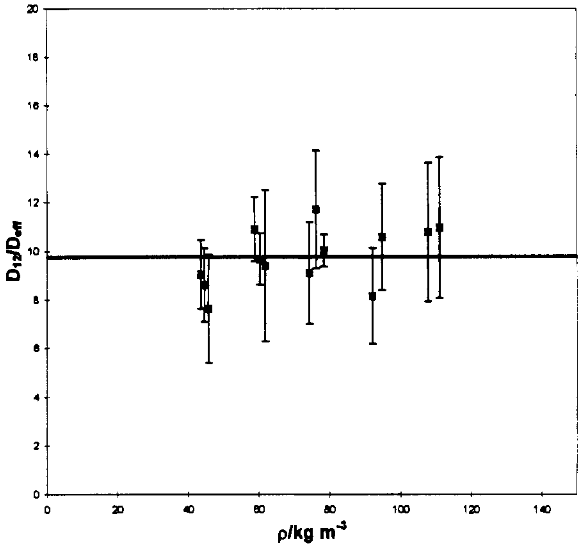

Figure 6. Dependency of τ/ϵ_p on solvent density.

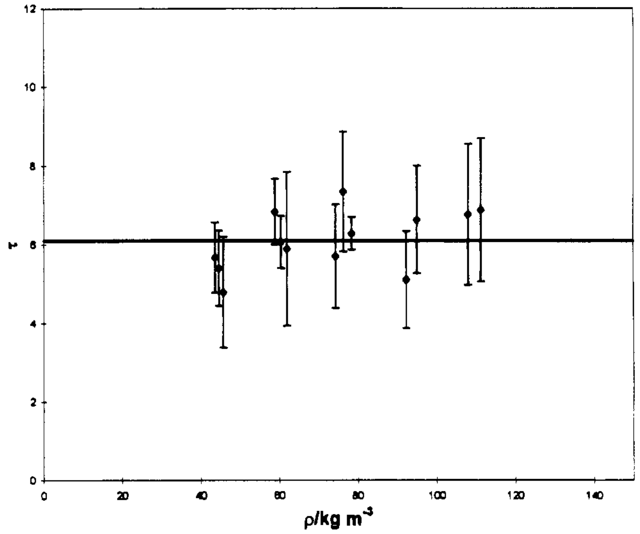

Figure 7. Dependency of τ on solvent density.

Conclusions

An impulse response technique using a subtraction of moments method was applied to determine the molecular diffusion coefficients and effective diffusivities of 1-octene in supercritical ethane at high temperatures. The adsorption equilibrium constants, effective diffusivities, and molecular diffusion coefficients have been measured for the 1-octene–ethane system over the temperature range of 523–543 K and at pressures in the realm of the reaction conditions. The tortuosity of the system was determined from the results of these experiments. It was shown that both the molecular diffusion coefficient and the effective diffusivity decreased with increasing density. Corresponding to this the tortuosity factor was relatively constant over the experimental range.

Notation

C = concentration in the fluid phase, mol/m^3
D_{12} = molecular diffusion coefficient, m^2/s
D_{ax} = axial dispersion coefficient, m^2/s
D_{eff} = effective diffusivity, m^2/s
d_p = particle diameter, m

K_A = adsorption equilibrium constant, m^3/kg
k_a = adsorption rate constant, m^3/(kg^3 s)
k_f = external mass transfer coefficient, m/s
L = length of the Taylor dispersion tube, m
L_t = length of the packed catalyst column, m
Pe = Peclet number, Ud_p/D_{ax}
R = inner radius of the Taylor dispersion tube, m
R_c = radius of the Taylor dispersion coil, m
R_t = inner radius of the packed catalyst column, m
t = time, s
t_r = residence time, s
U = interstitial velocity in the packed catalyst column, m/s
n = number of points obtained for the curve
i = point number

Greek Letters

ϵ_p = catalyst particle porosity
ϵ_b = catalyst bed porosity
τ = tortuosity
ρ_p = bulk catalyst particle density, kg/m^3
$\sigma_m{}^2$ = variance, s^2
μ_1 = first moment of the response curve, s
μ_2 = second moment of the response curve, s^2
μ_I = first moment of the input signal, s
μ_{II} = second moment of the input signal, s^2

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