Dynamic tracer method for the determination of effective liquid-phase diffusion coefficients and adsorption in continuous packed columns

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Highlights

- A tracer method was developed for the measurement of effective diffusion coefficients.
- The method is based on the step response experiments in columns.
- Experiments and mathematical modelling confirmed the feasibility of the approach.

1. Introduction

Many industrially relevant chemical processes are affected by liquid-phase diffusion resistance in porous materials, for example in heterogeneous catalysts. Therefore, reliable experimental methods for the determination of effective diffusion coefficients in porous structures are highly desirable. In this work, a method was developed to study the internal diffusion effects in porous media by step response experiments with tracers injected to fixed beds filled with porous particles and inert material.

2. Methods

Transparent glass columns filled with porous aluminum particles were used in the experiments. The tracer responses were recorded at the outlet of the bed by UV-vis spectrometry. Ethanol was used as an inert tracer and water as the solvent. The tracer responses were recorded at the outlet of the bed by UV-vis spectrometry. The packed column configurations are displayed in Figure 1.

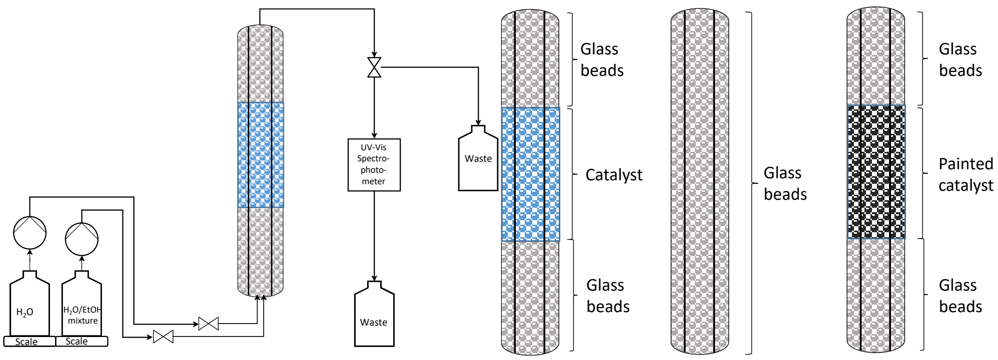

Figure 1. Experimental set up of the residence time distribution (RTD) experiments. View of the packed bed with sections: glass beads and catalyst (left), glass beads (centre), glass beads and painted catalyst (right). Painted (non-porous) catalyst particles were used for the determination of the axial dispersion coefficient.

For the adsorption-diffusion section, the balance equation (1) takes into account both the axial dispersion effects and the diffusion of the tracer into the pores of the solid material,

$$\frac{dc_{A2}}{dt} = D_{A2}\frac{d^2c_{A2}}{dl^2} - \frac{w}{\varepsilon_2}\frac{dc_{A2}}{dl} + \frac{N_A}{\varepsilon_P}a_P \qquad (1)$$

N_A is the interfacial flux at the outer surface of the catalyst particle, and N_A=-(D_{eA} c_A/dr) at $r=R$, where D_{eA} is the effective diffusion coefficient of the tracer and $a_P=A_P/V$, i.e. the ratio of the outer particle area-to-volume, which is assumed to be constant inside the bed. In case of adsorption equilibrium, the component mass balance inside the pores (P) can be expressed by equation (2),

$$\frac{dc_{AP}}{dt} = \frac{D_{eA}\left(\frac{d^2c_{AP}}{dr^2} + \frac{s}{r}\frac{dc_{AP}}{dr}\right)}{\varepsilon_P + \frac{K_A c_0 \rho_P}{(1+K_A c_{AP})^2}} \qquad (2)$$

3. Results and discussion

A comparison of the experimental and predicted curves of the tracer is provided in Figure 2.

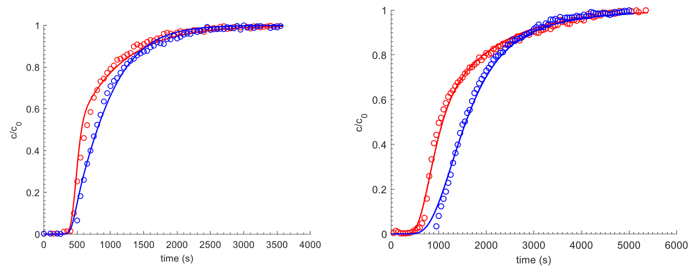

Figure 2. Experimental and modelling results of normalized step responses (c/c_0) of the tracer in the absence of catalyst (inert glass beads, red color) and in the presence of catalyst (blue color). Left: 50°C, 2mL/min; right: 25°C, 1mL/min. The difference between the responses represents the diffusion and adsorption effects.

The molecular diffusion coefficient of ethanol in a dilute aqueous solution can be estimated from correlations given, for example by Wilke and Chang and Scheibel [1-2]. The correlation proposed by Wilke and Chang proposes (A= ethanol and B= water),

$$\frac{D_A}{m^2/s} = 7.4*10^{-12}\frac{(\Phi_B M_B)^{1/2}T}{\mu_B V_A^{0.6}}$$

For water M_B=18 g/mol, φ_B=2.6 (the association factor for water). The molar volume at the normal boiling point is estimated from the atomic increments of Le Bas (A=ethanol= C_2H_5OH), V_A== 2*C+6*H+ 1*O=2*14.8+6*3.7+7.4= 59.2cm^3/mol, which gives the proportionality factor

$$7.4*10^{-12}\frac{(\Phi_B M_B)^{1/2}}{V_A^{0.6}} = 7.4*10^{-12}\frac{(2.6*18)^{1/2}}{59.2^{0.6}} = 4.37483444*10^{-12}$$

$N_A a_P$=-D_{eA} a_P (c_A/dr), i.e. appears as a merged parameter in the model equation. At 25°C, the product $D_{eA}a_P$ was determined by parameter estimation to 0.486 10^{-6}m/s, whereas the product $D_A a_P$ based on the molecular diffusion coefficients is 1.534 10^{-6}m/s ($a_P=\pi/(2R_P)$). These results give the ratio between the molecular and effective diffusion coefficient 0.486/1.534=0.32, which is a reasonable result, considering that the mean transport pore model predicts that $D_{AeA}/D_A=\varepsilon_P/\tau_P$, i.e. less than 1.

4. Conclusions

The step response experiments with the packed bed filled porous catalyst particles demonstrated the feasibility of the proposed method for the determination of effective liquid-diffusion coefficients in porous media. Mathematical modelling was carried out successfully and we were able to estimate the numerical values of the effective diffusion coefficients by comparing the step responses obtained with porous aluminum oxide particles, painted non-porous particles and with inert glass particles. Further research should be devoted to scale down the equipment to be able to operate with smaller amounts of particles and with structured catalysts, such as monoliths, solid foams, and 3D printed structures.

References

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Keywords

Effective diffusion coefficient, packed column, tracer, step response experiments