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Moments Method Applied to the In-Situ Characterisation of Normal Butane Mass Transfer in MFI Zeolite Membranes

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1. Introduction

Modelling the mass transfer through a zeolite membrane is a complex task. Indeed, it is widely admitted that the local effective diffusion coefficient of adsorbed species in zeolite strongly depends on their local concentration. Thus, it is virtually impossible to uncouple thoroughly diffusion and adsorption data from a single experimental result, i.e. the steady-state partial flux of each permeating species. As in situ adsorption isotherm data measurements can hardly be done with a composite zeolite membrane sample, we propose in the present work an original membrane characterisation method, based on a transient measurement technique applied in the linear response domain.

The goal of this study was to check if the characterization of the diffusion process of normal butane in MFI membranes could be validated experimentally.

2. Principle & modeling for the moments method

The transient technique is based on the perturbation chromatography technique commonly called Concentration Pulse Chromatography [2]. Applied to membranes, the basic principle of this method [3] consists in performing a concentration pulse of a component, at time zero and at the inlet of a membrane. The initial thermodynamic and thermal equilibrium is thus perturbed, producing an outlet concentration evolution on each side of the membrane.

When in contact with the Dirac pulse, the adsorbate concentration variation inside and at the surfaces of the membrane is low enough one may assume that: (i) the mass transfer inside the membrane is isothermal, (ii) the adsorption equilibrium remains linear and (iii) the effective diffusion coefficient remains constant all over the membrane thickness. Under these conditions, a linear mass transfer model, valid only in the neighbourhood of the initial equilibrium state, was used. This assumption was experimentally validated by a comparison of the measured outlet concentration profiles of different n-C$_4$ pulse composition tests. A rather satisfying superposition of the curves is observed (see figure 1) which

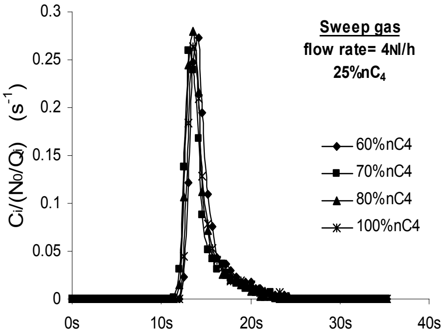

Figure 1. Normalised retentate concentration response at the outlet of the membrane (1 atm, 200 °C)

means that the transfer parameters remain constant and that the domain can be considered as linear.

As the concentration variation on both sides of the membrane is infinitely small, the mass transfer can be described by the Fick equation and the equilibrium relationship between the gas phase and the adsorbed phase is also assumed to be linear. For a non-linear adsorption isotherm, K is the adsorption curve slope at the initial equilibrium conditions. Thanks to linearity conditions, it is possible to solve the mass balances in the Laplace domain. B_m and θ_m are the two groups of parameters related to the zeolite layer properties that appear in the two transfer functions between the inlet inner compartment concentration and the two measured outlet concentrations. After some tedious calculations, one can obtain the theoretical expressions of the zero and first order moments. A series of experiments was realised for three different sweep gas concentrations corresponding to three different points of the adsorption isotherm. The comparison of the experimental values of the moments with the theoretical expressions allows to estimate the parameters B_m and θ_m (table 1), the results are listed in table 1.

Ke_z can be determined by calculating the following ratio: $B_\mathrm{m}/\theta_\mathrm{m}=K.e_\mathrm{z}$. In a subsequent stage of the study, transient experiments will be performed with a non-adsorbing tracer [3], so that e_z can be estimated independently of K. Once the zeolite layer thickness is known, the estimated values of θ_m and B_m obtained with normal butane will allow to determine D_m and K for this component at several partial pressures.

Table 1. Parameter groups obtained with the first and zero order moments (1 atm, 200 °C)

	mean value of $B_m=K.D_m/e_z$	mean value of $\theta_m= D_m/e_z^2$
0% nC_4	0.000858m/s	0.0600s-1
25% nC_4	0.000434m/s	0.0939s-1
50% nC_4	0.000224m/s	

3. Conclusion

It has been shown in the present study that it is possible to characterise thoroughly the mass transport of an adsorbing light hydrocarbon through a tubular zeolite membrane (normal butane through a MFI zeolite membrane) by measuring its transient mass flux induced by a Dirac concentration stimulus. As it was proven experimentally that the response of the studied system was linear with respect to the stimulus (very low concentration perturbation), it was possible to extract parameter groups from the experimental data with a simplistic mass transfer model which allowed to calculate two parameter groups, $KD_\mathrm{m}/e_\mathrm{z}$ and $D_\mathrm{m}/e_\mathrm{z}^2$. Provided that the effective thickness of the zeolite layer is known by other means, these parameter groups are able to give the adsorption equilibrium constant, and the diffusion coefficient of the adsorbate in the zeolite membrane separately. When this point is solved, it is eventually planned to study the mass transfer of a slowly permeating compound (i.e. isobutane) and extend this method to studying the mass transfer of normal butane / isobutane mixtures.

References

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