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Kinetic separation of CO₂ and CH₄ on Carbon Molecular Sieves: Study of the internal diffusion and surface resistance of pure gases and binary gas mixtures

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Introduction and objectives

Carbon Molecular Sieves (CMS) appear to be good candidates for gas kinetic separation by using Pressure Swing Adsorption (PSA) processes. Their pore morphologies could imply diffusion rate variations depending on their nature and the steric size of the adsorbate. We thus propose to analyze the different mechanisms involved during the adsorption/desorption of pure CO₂, pure CH₄, and their mixtures by using the Zero Length Column (ZLC) theory: the aim of the approach is to quantify the intraparticle diffusion resistance [1]. But recent studies pointed out that the surface resistance could be significant and could control the rate of adsorption [2]. The ZLC theory has thus been extended to the analysis of both intraparticle and external surface resistances determination [3-4]. The ZLC method is a macroscopic approach which allows to separate these different resistances by adjusting gas velocities in a column containing a small amount of adsorbent. Pure CO₂ desorption rate measurements are performed to quantify the effective diffusivity of CO₂ in the CMS material. Then the desorptions of binary mixtures of CO₂ and CH₄ are performed by adjusting the rate of CH₄ in the mixture to evaluate its influence on the desorption of CO₂, and to separate intraparticle diffusion resistance and surface resistance contribution.

Zero Length Column (ZLC) theory

ZLC experiment are carried out by preequilibrating a small sample of adsorbent with a steam at a low concentration of the adsorbable compound in He carrier, and then by desorbing the adsorbable compound in pure He steam

Hypotheses

- ZLC cell well mixed
- Linear adsorption equilibrium between fluid and adsorbed phases
- Constant diffusivity (do not depend on the internal adsorbed phase concentration)
- Spherical adsorbent particles
- Desorption controlled by intraparticle diffusion

Mass balance:
$$\frac{\partial q}{\partial t} = D_{eff} \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (1)$$

Initial conditions:
$$t < 0: q = q_0 = Kc_0 \quad \forall r \quad (2)$$

Boundary conditions:
$$r = 0: \left(\frac{\partial q}{\partial r} \right)_{r=0} = 0 \quad (3)$$

$$r = R: -D_{eff} \left(\frac{\partial q}{\partial r} \right)_{r=R} = \frac{QR}{3KV_s} q_R = \frac{QR}{3V_s} c(t) \quad (4)$$

Analytical solution:
$$\frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp(-\beta_n^2 D_{eff} t / R^2)}{[\beta_n^2 + L(L-1)]} \quad (5)$$

Where β_n^2 is given by the roots of:
$$\beta_n \cot \beta_n + L - 1 = 0 \quad (6)$$

And L is defined as:
$$L = \frac{Q}{3KV_s D_{eff}} R^2 = \frac{1}{3} \frac{\text{purge flow rate}}{\text{adsorbent volume}} \frac{R^2}{D_{eff}} \quad (7)$$

For large values of t , then only the first term of the equation (5) is significant, and for large values of L , then $\beta_1 \rightarrow \pi$:

$$\ln \left(\frac{c}{c_0} \right) \approx \ln \left[\frac{2L}{\pi^2 + L(L-1)} \right] - \pi^2 \frac{D_{eff} t}{R^2} \quad (8)$$

With surface resistance:

Change of the boundary condition

$$r = R: -D_{eff} \left(\frac{\partial q}{\partial r} \right)_{r=R} = k(q_R - q_{surf}) = \frac{QR}{3KV_s} q_{surf} = \frac{QR}{3V_s} c(t) \quad (9)$$

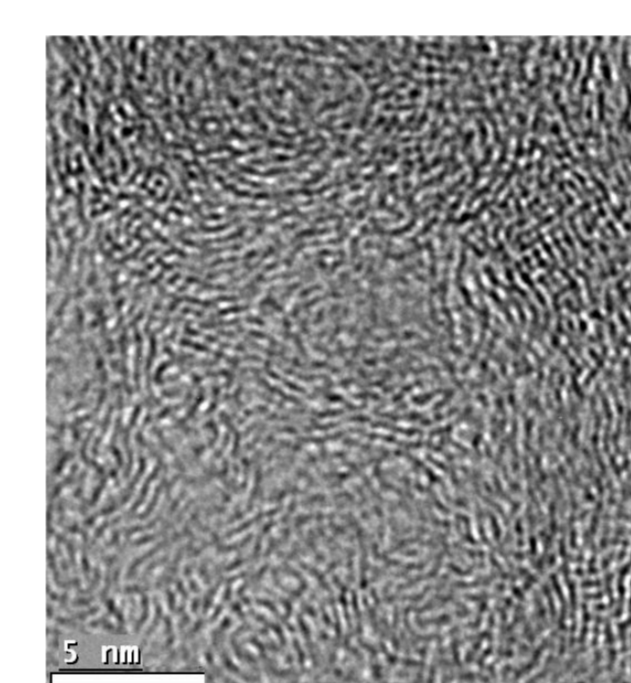
Expression of the apparent L' :

$$\frac{1}{L'} = \frac{1}{L} + \frac{D_{intra}}{kR} \quad (10)$$

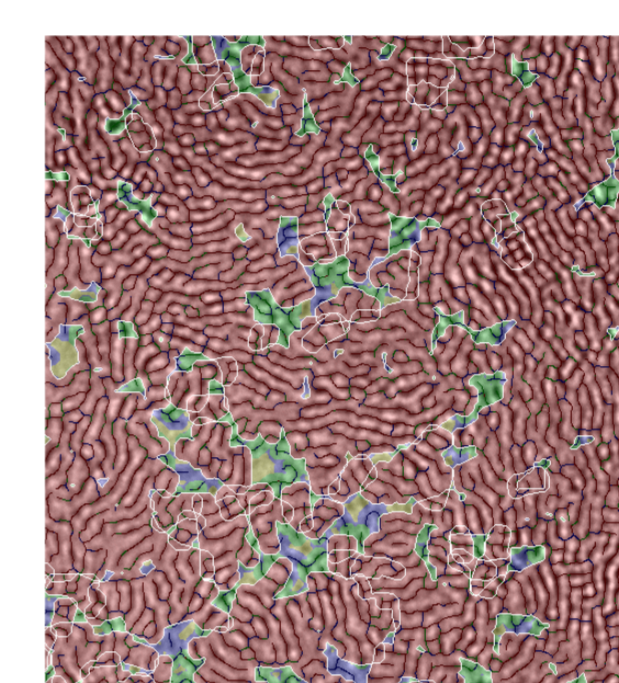
Apparent L' (obtained from effective diffusivity) ← Intraparticle diffusion contribution ← External resistance contribution

Characterization of the CMS

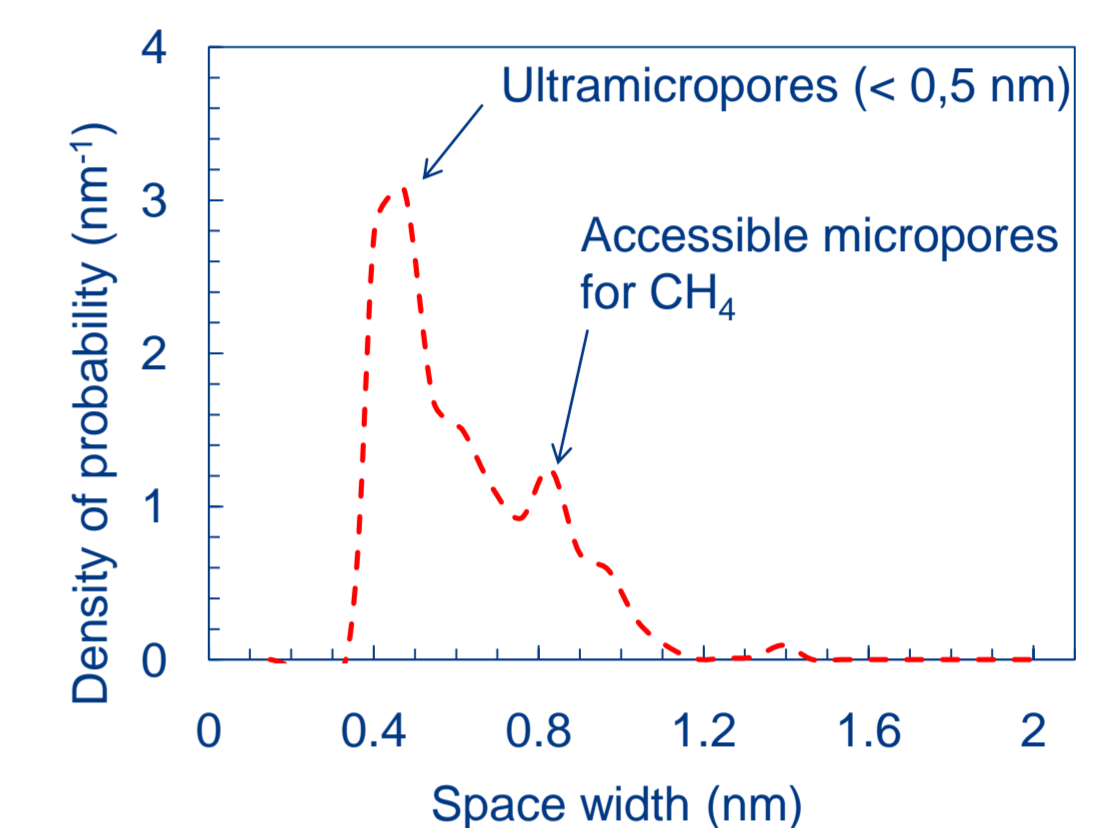
CMS is provided by CarboTech. Its micropore volume is obtained by CO₂ adsorption isotherm measurement at 273 K: 0.22 cm³ g⁻¹ for pore diameters smaller than 0.7 nm. The SEM analysis of the microstructure shows the different pore morphologies [5].



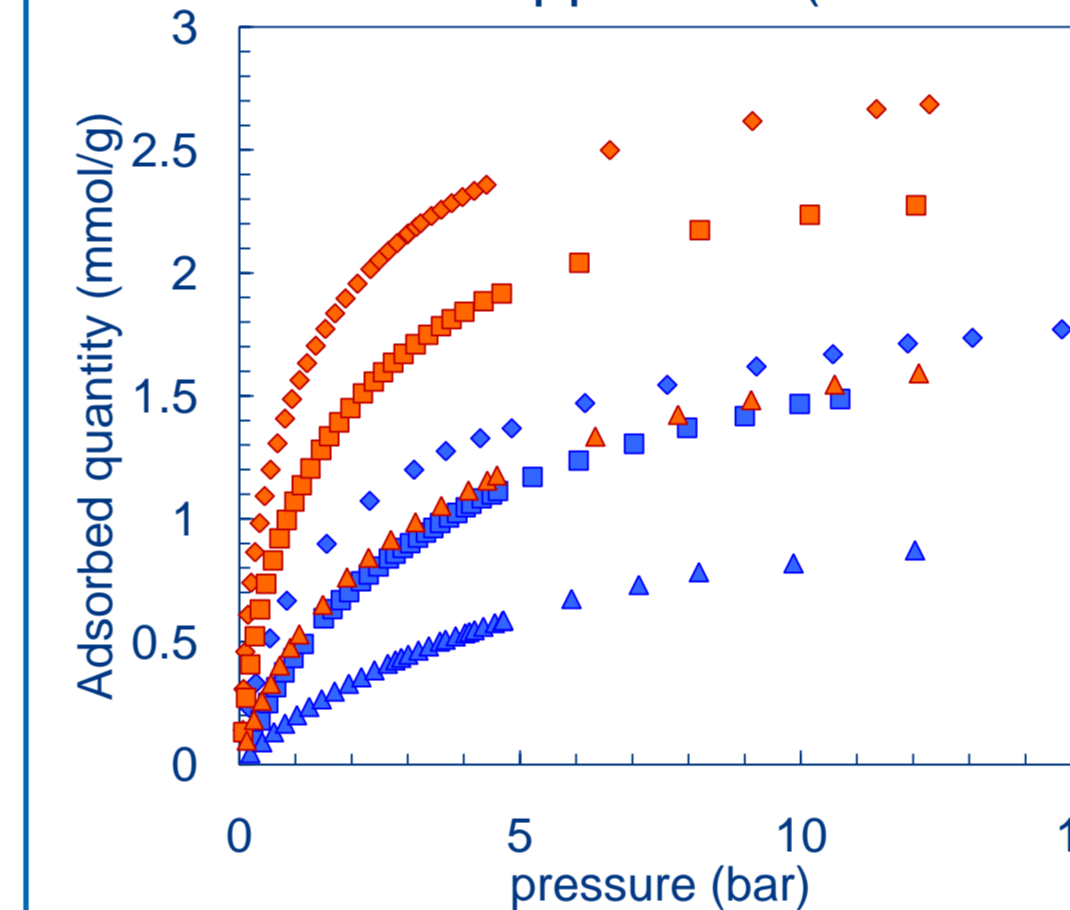
Raw picture



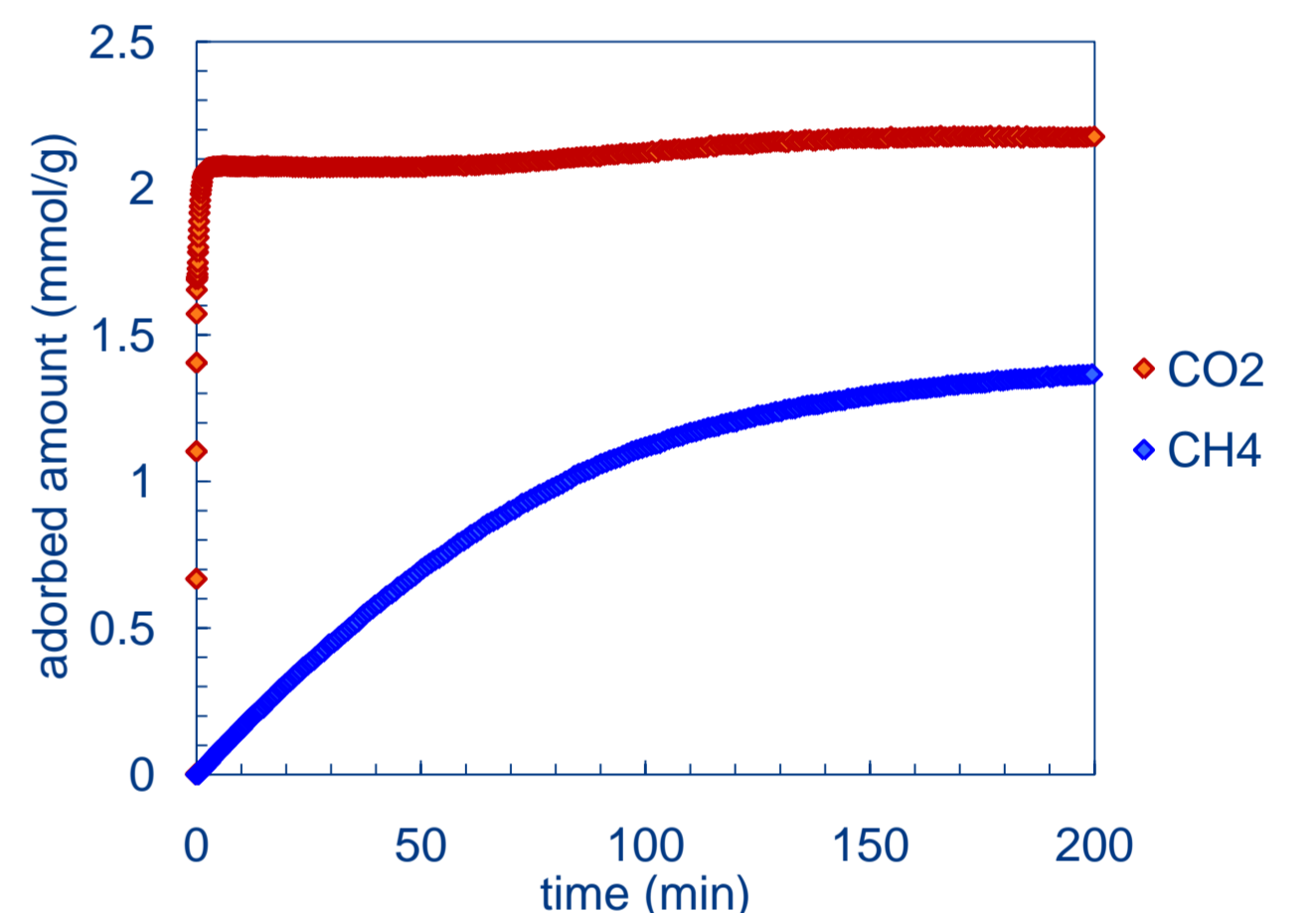
Red: continuous domains
Blue: single fringes
Green: layer stacks



Pure CO₂ and CH₄ isotherms using a manometric apparatus (PCT Pro by Setaram)



uptake curves of pure CO₂ and pure CH₄, from 0 bar to 5 bar at 303 K



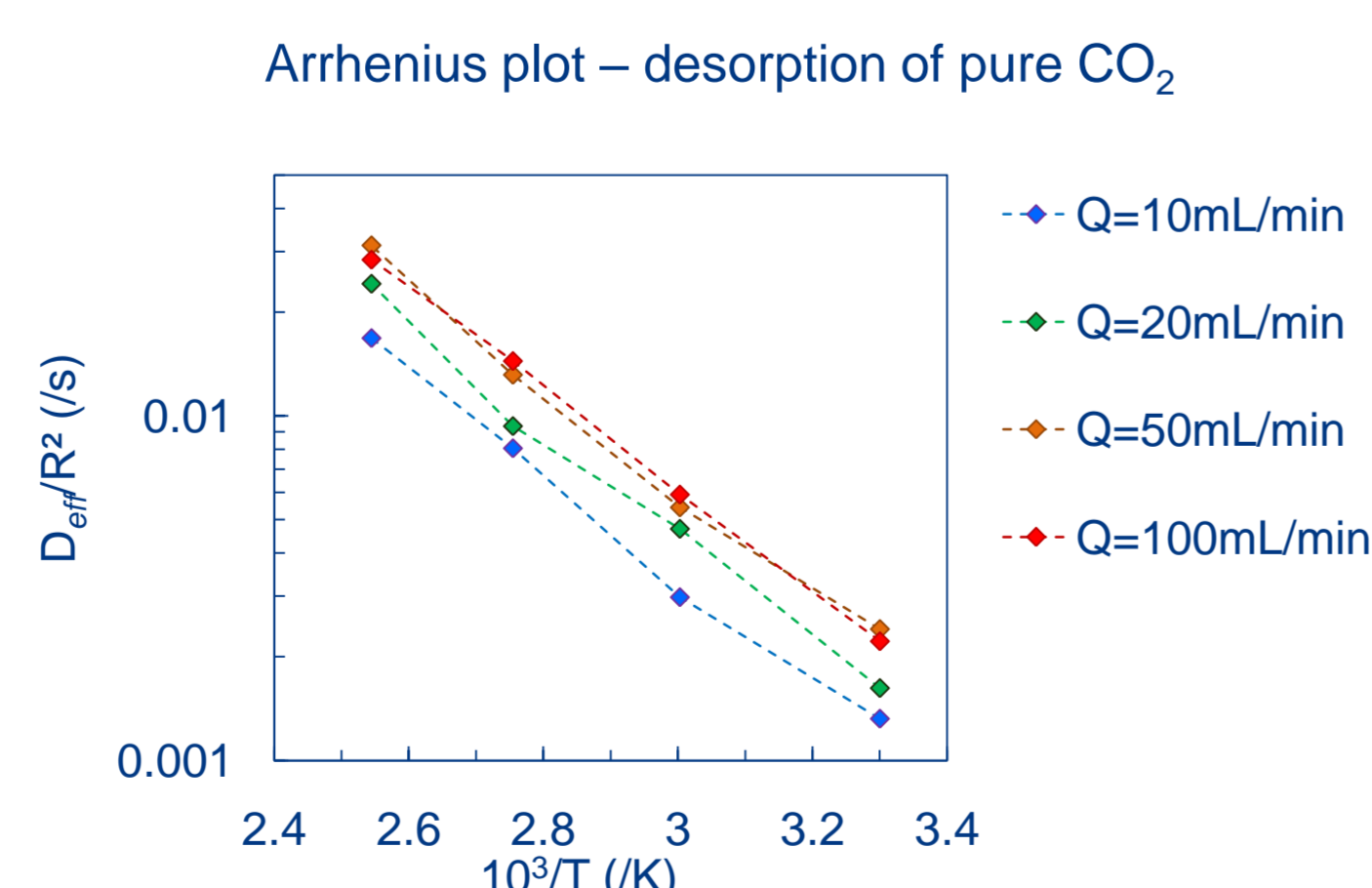
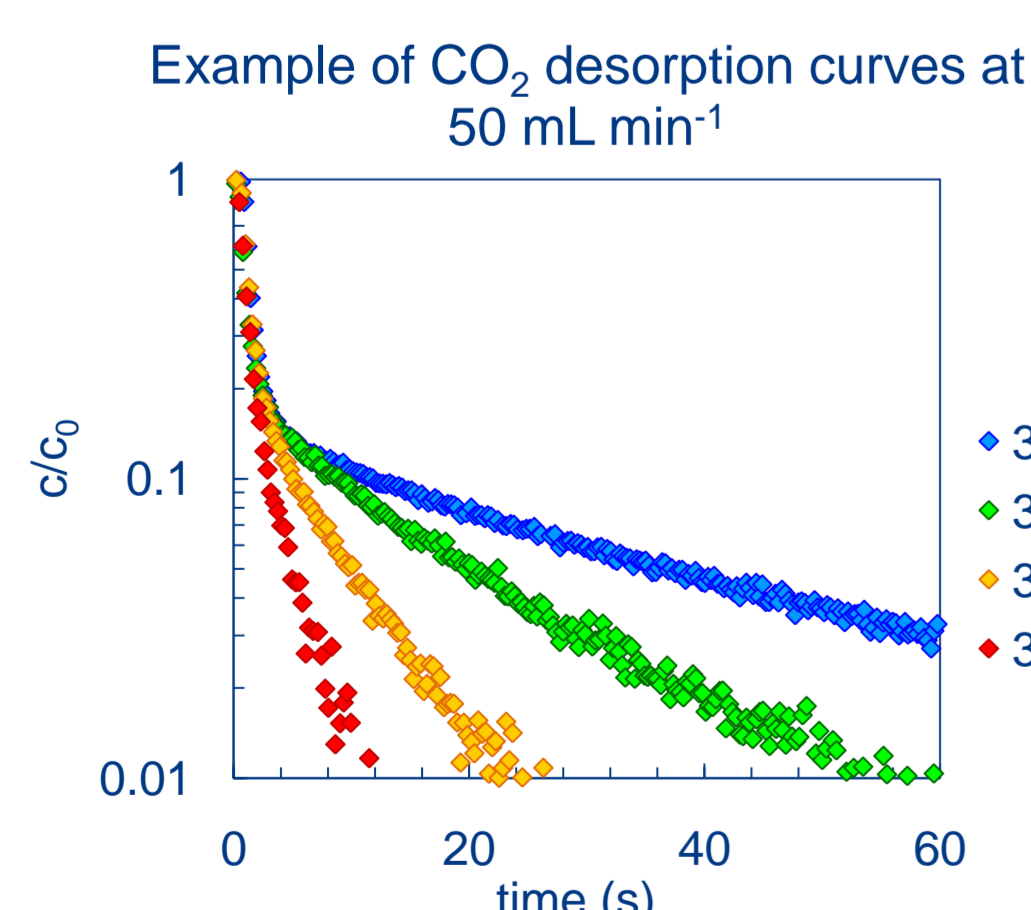
Temperature (K)	Langmuir model		Henry model	
	Saturation quantity (mmol g ⁻¹)	Affinity constant (bar ⁻¹)	K (mmol g ⁻¹ bar ⁻¹)	
CO ₂	303	2.81	1.12	15.1
	323	2.52	0.70	2.16
	363	1.99	0.32	0.60
CH ₄	303	2.02	0.47	1.03
	323	1.98	0.28	0.56
	363	1.37	0.16	0.20

From uptake curves, the CO₂ adsorption is a very fast phenomenon whereas the adsorption of CH₄ is slow due to the exclusion of CH₄ molecules.

Pure CO₂ desorption experiments

Carried out on a home-made apparatus similar to the one developed by Eic and Ruthven [1] with a constant partial pressure of 5 kPa of CO₂ in the He matrix (total pressure of 1 atm). 45.5 mg of CMS has been used for these experiments.

1. D_{eff}/R^2 are obtained from the slope of the desorption curve in the long time region (equation 8).
2. Determination of the kinetic regime for different gas velocities (from 10 to 100 mL min⁻¹) and for temperature from 303 K up to 393 K

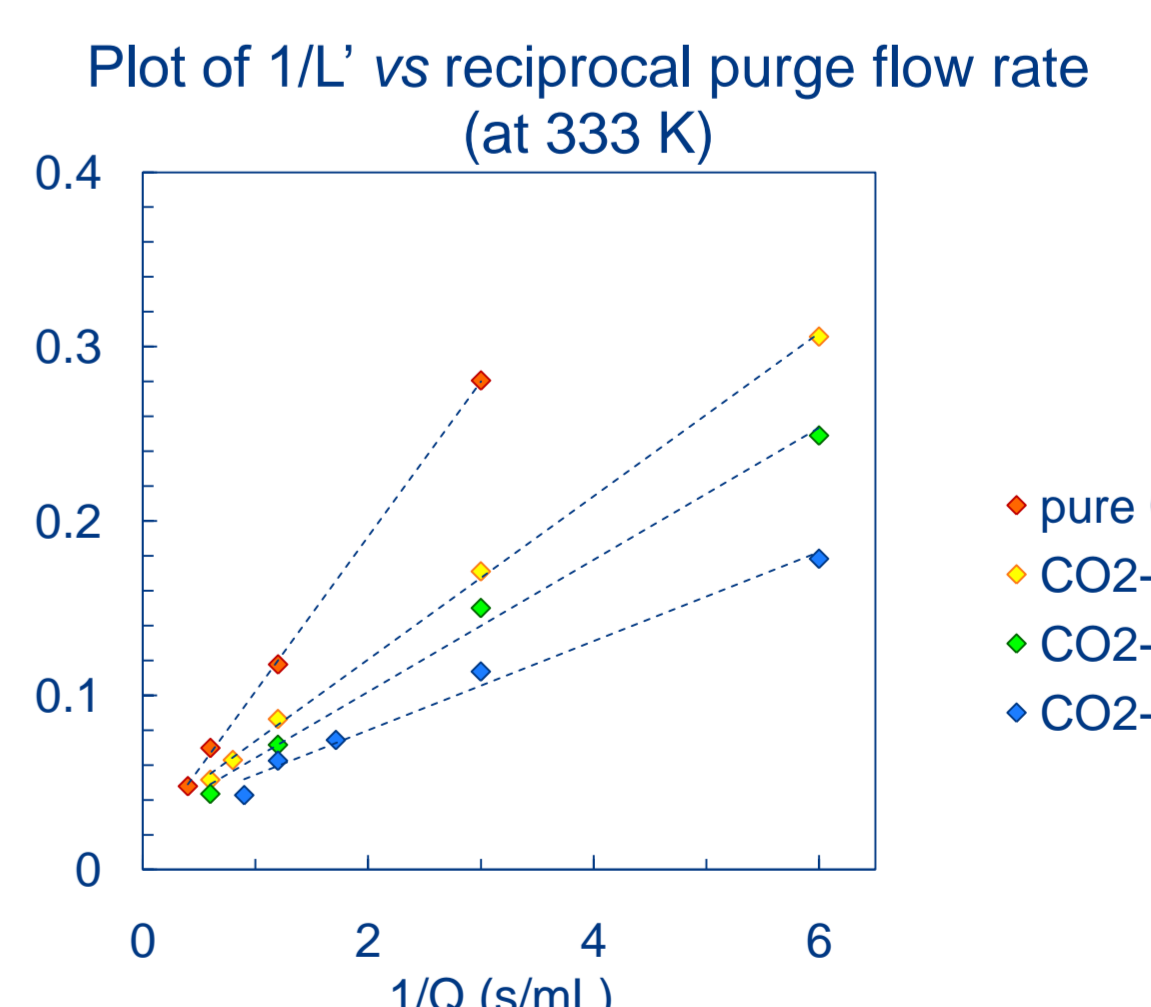
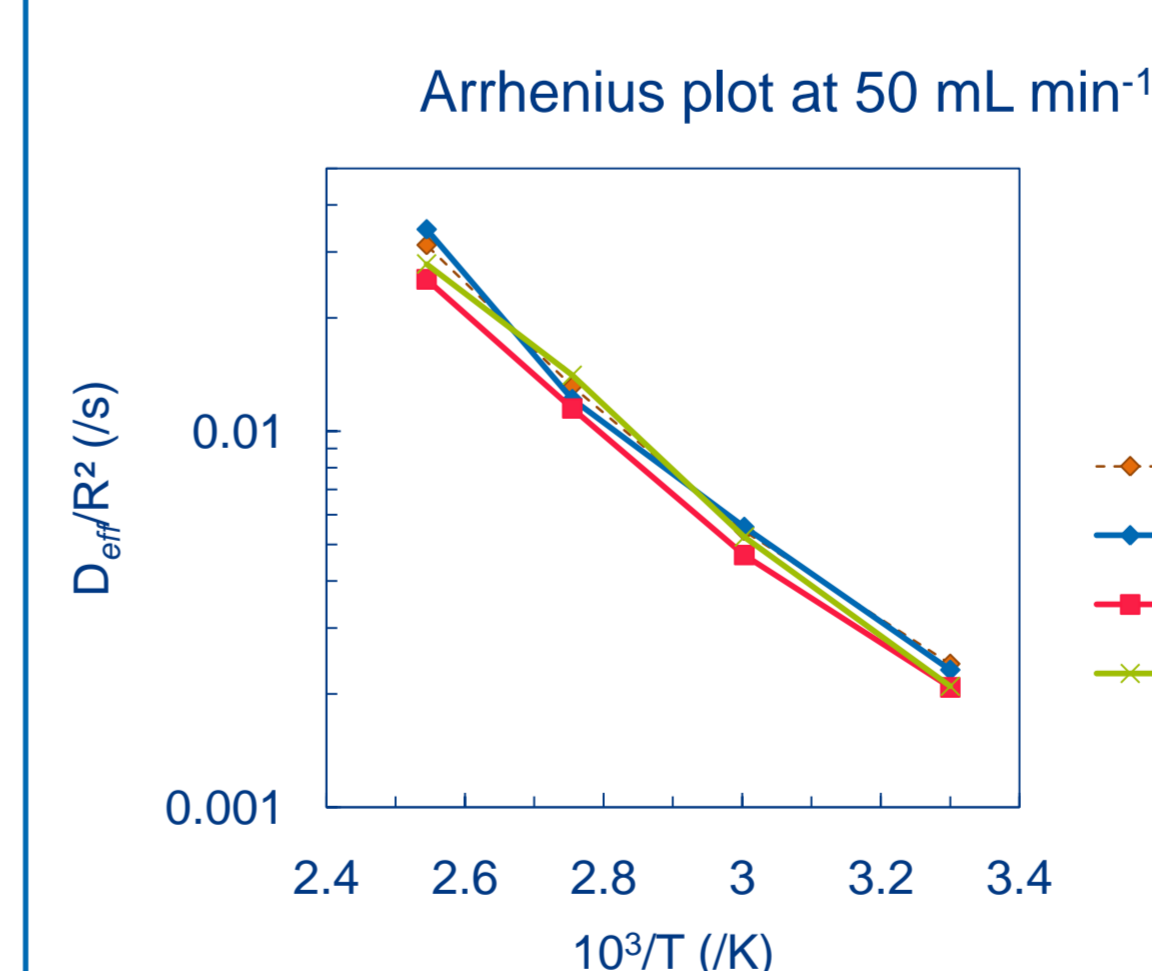


The kinetic regime is reached for gas velocities greater than 50 mL min⁻¹:

- <50 mL min⁻¹: both thermodynamics and kinetics controls
- >50 mL min⁻¹: constant diffusivity independent of the gas flow velocity, i.e., kinetics control

CO₂-CH₄ mixtures desorption experiments

Constant partial pressure of CO₂ of 5 kPa and variation of CH₄ partial pressure to give CO₂-CH₄ mixtures 67-33, 50-50, and 33-67. The desorption of CH₄ is too slow to be analyzed: the MS detector does not allow to measure it.



From Arrhenius plot, there is no evidence of the effect of the CH₄ on the effective diffusivities whatever the temperature.

From the plot of $1/L'$ as a function of $1/Q$, the decrease of the slope when CH₄ concentration increases corresponds to a decrease of the intraparticle CO₂ diffusivity. However the ratio of the intraparticle diffusivity over the external resistance mass transfer (k) explained by the y-intercept keeps constant whatever the CH₄ concentration.

Conclusion

This study focuses on the separation of the intraparticle diffusion of CO₂ and the surface resistance contribution. When increasing the CH₄ amount, the contribution of the CO₂ intraparticle diffusion decreases whereas the CO₂ mass transfer coefficient at the external surface increases: the adsorb CH₄ contributes to slow the intraparticle CO₂ diffusivity but also contributes to accelerate the mass transfer in the surface zone. We thus show that, through the framework of CO₂-CH₄ kinetic separation using a CMS adsorbent, it is important to consider the effect of the concentration of CH₄ when determining the CO₂ diffusivity.

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