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Permeation time lag with multilayer adsorption and surface diffusion

S.W. Rutherford, D.D. Do*

Department of Chemical Engineering, The University of Queensland, St. Lucia, Qld 4072, Australia

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Abstract

Analysis of the permeation of adsorbed molecules through a carbon pellet has been undertaken in order to investigate the dependence of the adsorbed phase mobility upon the concentration of the adsorbed phase. The dependence is shown to be described well by the model proposed by Chen and Yang [Y. Chen, R.T. Yang, Carbon 36 (10) (1998) 1525] which can apply to adsorbed phase concentrations greater than that at saturation but still within the BET limits. The time lag for permeation is also shown to provide a useful and reliable means for investigating the adsorbed phase diffusion process. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

Investigation of the process of adsorbed phase diffusion has been ongoing since the origin of research into the adsorption phenomena. Despite much effort, the fundamental understanding of the phenomena is still incomplete. This is probably due to the complexity of the interaction between the fluid and the solid that accompanies the phenomena. The need for fundamental investigation into this phenomena stems from the fact that it intrudes into many fields of science and technology [1]. The gas permeation technique is a useful method for investigating the phenomena. Most commonly used is the steady state permeation technique. Less commonly used is the time lag permeation method where steady state information is obtained simultaneously with transient information usually presented in the form of the 'time lag'. This time lag for permeation also carries information about the mobility of the permeating phases. In order to extract this information, the method of [2] is utilised. The information extracted usually presents itself in the form of a relationship between the mobility and the adsorbed phase concentration. Many such relationships have been proposed in the literature. Some have been presented in the review by [3]. Most of the relationships predict the dependence based upon the shape of the isotherm. Recently, several different approaches have been presented. Thermodynamic and hydrodynamic interpretations have been used [4] as well as interpretation based on transition state theory [5]. For materials with a wide pore size distribution network effects are also incorporated [6,7]. In this paper we analyse the relationship between the mobility and the adsorbed phase concentration at concentrations higher than that at saturation but within the BET limits. We use the model proposed by [5] to describe the mobility. The measured time lag is analysed and the method of [2] is used to determine the relationship between time lag and mobility.

1.1. Permeation system

Measurement of the permeation rate and time lag is conducted by maintaining a source volume at constant concentration while the concentration in a sink volume is monitored. After some time the permeation rate will approach a constant value. Further discussion of the experimental details can be found in a review by [9].

1.2. Mass balance

The mass balance for the diffusion process through a porous solid when adsorption (with local equilibrium) and diffusion of the adsorbed phase occurs simultaneously with the gas phase is represented as

$$\varepsilon\frac{\partial C}{\partial t}+\varepsilon_\mu\frac{\partial C_\mu}{\partial t}=\frac{\partial}{\partial x}\left(\varepsilon D_\mathrm{e}\frac{\partial C}{\partial x}+\varepsilon_\mu D_\mu\frac{\partial C_\mu}{\partial x}\right) \tag{1}$$

where the C represents the concentration in the gas phase (mole per unit volume gas phase), C_μ represents the concentration in the adsorbed phase (mole per unit volume adsorbed phase), ε_μ represents the volume fraction of the pellet attributable to the adsorbed phase and ε represents that attributable to the gas phase.

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*Corresponding author. Tel.: +61-7-336-54154; fax: +61-7-336-54199.

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When the two phases are in local equilibrium with each other, Eq. (1) can be cast into the following form

$$\left(\varepsilon + \varepsilon_\mu \frac{\partial C_\mu}{\partial C}\right)\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(H\frac{\partial C}{\partial x}\right) \tag{2}$$

where the function H is defined as

$$H = \varepsilon D_\mathrm{e} + \varepsilon_\mu D_\mu \frac{\partial C_\mu}{\partial C} \tag{3}$$

The measure of the gas phase mobility is the effective diffusivity D_e. While the gas phase diffusion mechanism is one of Knudsen diffusion, the effective diffusivity remains constant. It is usually evaluated through measurement of non-adsorbing helium permeation. The measure of the adsorbed phase mobility is the adsorbed phase diffusivity D_μ which is only constant when the amount adsorbed is very low.

When a constant upstream concentration (C_0) is applied and the downstream concentration is kept to a value negligible in comparison to the upstream, the permeation process will reach a steady state after some time delay. The time delay is known in the literature as the 'time lag' which in itself provides useful kinetic information related to the mobility of the diffusing species. [2] showed that the measurable time lag can be related to the diffusivity by manipulating the mass balance equation. A general form for the time lag which includes adsorption and surface diffusion can be obtained by using his procedure. The result is

$$t_\mathrm{lag} \frac{L^2 \int_0^{c_0} \left(\varepsilon C + \varepsilon_\mu C_\mu\right) H(u) \left(\int_u^{c_0} H(w)\,\mathrm{d}w\right)\mathrm{d}u}{\left(\int_0^{c_0} H(u)\,\mathrm{d}u\right)^3} \tag{4}$$

It is obvious from (Eq. (4)) that if the dependence of the function H upon the concentration is known and that the dependence of the adsorbed phase concentration upon the gas phase concentration is known (ie. isotherm is known), the time lag can be evaluated.

1.3. Adsorbed phase

The presence of adsorption in the permeation process has the effect of elongating the time delay between the commencement of the diffusion process and the time at which a steady state transfer is achieved. If the adsorbed molecules exhibit some degree of mobility, this will reduce the time delay. The net effect of both these factors is determined by the relative pore and surface diffusion rates.

When dealing with very low relative pressures a linear isotherm results and the mass balance can be solved analytically for the downstream pressure rise. At higher relative pressures where the isotherm is non linear, the mass balance cannot be solved analytically. The time lag has been used as simple means for characterisation for concentrations less than monolayer coverage [8,9]. Above monolayer coverage, the BET equation is useful in the description of the adsorption isotherm

$$\theta = \frac{C_\mathrm{BET} P/P_\mathrm{v}}{(1 - P/P_\mathrm{v})(1 - P/P_\mathrm{v} + C_\mathrm{BET} P/P_\mathrm{v})} \tag{5}$$

where θ is the fractional loading ($\theta = C_\mu / C_{\mu\mathrm{s}}$), P_v the vapour pressure and c_BET is the BET constant. The time lag can be used for characterisation above saturation (as it has for concentrations below saturation) once a relationship between the surface diffusivity and the adsorbed phase concentration is established.

1.4. Dependence of the surface diffusivity

At low relative pressures, the isotherm is linear and the adsorbed phase diffusivity is essentially independent of the adsorbed phase concentration. At higher relative pressures, where the isotherm is non-linear, the diffusivity generally increases with loading. The Darken equation has been widely used to describe the dependence of the mobility of the adsorbed phase upon loading. This has proven to be useful for the diffusion of supercritical gases or vapours at low relative pressures where the adsorbed phase concentration is less than the monolayer concentration. However, when dealing with higher relative pressures where the monolayer capacity is exceeded, the mobility of the adsorbed phase rises to reach a maximum around monolayer coverage, and is then followed by a decrease as the relative pressure increases. [5] have used transition state theory to describe this dependence and have successfully applied the theory to available literature data. The relationship is as follows,

$$\frac{D_\mu}{D_{\mu 0}} = \frac{1 - P/P_\mathrm{v} + (P/P_\mathrm{v}\alpha)}{1-(1- P/P_\mathrm{v})\theta + (\alpha(1- P/P_\mathrm{v})\theta^2/1- (1- P/P_\mathrm{v})\theta)} \tag{6}$$

where $D_{\mu 0}$ is the diffusivity at zero loading and α represents the ratio of the rate constants for adsorption of the first layer and higher layers. This relationship allows for the observed increase to monolayer coverage and subsequent decrease.

1.5. Steady state slope and profile

When the permeation process reaches a steady state, the rate of downstream pressure rise approaches a constant value and the concentration profile along the pellet becomes steady with respect to time. The mass balance at steady state becomes

$$\frac{\partial}{\partial x}\left(H\frac{\partial C}{\partial x}\right) = 0 \tag{7}$$

Subject to the constant boundary conditions of C_0 at the upstream face of the pellet and zero (negligible compared to the upstream concentration) at the downstream face, the solution of Eq. (7) gives the following concentration profile

$$1 - \frac{x}{L} = \frac{\int_0^C H(C)\,\mathrm{d}C}{\int_0^{C_0} H(C)\,\mathrm{d}C} \tag{8}$$

Using the BET Eq. (5) and the description of [5] Eq. (6), the function H (from Eq. (3)) takes the following explicit form:

$$H(C) = \varepsilon D_{\mathrm{e}} + \varepsilon_{\mu} D_{\mu 0} c_{\mathrm{BET}} C_{\mu \mathrm{s}} \frac{(C_{\mathrm{v}}^2 - C^2 + c_{\mathrm{BET}} C^2)(\alpha C_{\mathrm{v}} - \alpha C + C)}{\alpha (C_{\mathrm{v}} - C + c_{\mathrm{BET}} C)(C_{\mathrm{v}}^3 - 3C_{\mathrm{v}}^2 C + 3C_{\mathrm{v}} C^2 - C^3 + \alpha c_{\mathrm{BET}}^2 C_{\mathrm{v}} C^2)} \tag{9}$$

A common method to measure the combined adsorbed phase and gas phase mobility is to simply note the slope of the linear pressure rise at steady state. We refer to this as the steady state slope and the general form is given as

$$S_{\infty} = \frac{A}{L} \int_{0}^{C_0} H(C)\, \mathrm{d}C \tag{10}$$

Along with the steady state slope, the time lag also gives a measure of the mobility of the combined gas and adsorbed phases but both have differing dependence upon the diffusivity and concentration. For this reason it is useful to couple the two measurements where possible, to determine the diffusivity.

1.6. Time lag

Using the BET isotherm of Eq. (5) and the relation of [5] Eq. (6), it is possible to obtain an expression for the time lag, written in the following quadrature form:

$$t_{\mathrm{lag}} = \frac{L^2}{D_{\mathrm{e}} \left[\int_0^1 N(y)\, \mathrm{d}y \right]^3} \int_0^1 N(u) \times \left[u + \frac{\kappa c_{\mathrm{BET}} \lambda \phi u}{(\phi - u)(\phi - u + c_{\mathrm{BET}}\, u)} \right] \left[\int_u^1 N(w)\, \mathrm{d}w \right] \mathrm{d}u \tag{11a}$$

where

$$N(y) = 1 + \kappa \eta\, c_{\mathrm{BET}}\, \lambda \frac{(\phi^2 - y^2 + c_{\mathrm{BET}} y^2)(\alpha \phi - y\alpha + y)}{\alpha (\phi - y + c_{\mathrm{BET}}\, y)(\phi^3 - 3\phi^2 y + 3\phi y - y^3 + \alpha c_{\mathrm{BET}}^2\, y \phi y^2)} \tag{11b}$$

The parameters of the above equation are defined in Table 1.

Eqs. (11a) and (11b) clearly show that the time lag is dependent upon the pellet properties (L,ε), adsorbate properties (P_{v}), isotherm properties ($C_{\mu \mathrm{s}}$, c_{BET}) and experimental conditions (P,T). In order to evaluate the gas phase diffusivity, measurement of the helium permeation rate is undertaken. Independent evaluation of the isotherm usually compliments this result. This leaves only the adsorbed phase diffusivity and parameter α to be evaluated from the permeation experiment. When the time lag is measured for various upstream concentrations, Eqs. (11a) and (11b) can be used to predict the relationship and the two parameters can be evaluated by error minimisation. To improve the accuracy of the procedure, this can be performed at several temperatures.

Table 1
Definition of non-dimensional parameters

Parameter	Definition
κ	$\varepsilon_{\mu}/\varepsilon$
η	$D_{\mu 0}/D_{\mathrm{e}}$
λ	$C_{\mu \mathrm{s}}/C_0$
ϕ	$P_{\mathrm{v}}/(C_0 RT)$

We will apply this procedure to the measurement obtained by [10] of SO_2 permeation through a porous Carbolac I pellet whose details are summarised in Table 2.

The adsorption equilibrium measurement has been conducted and the amount adsorbed versus relative pressure is plotted by [10]. We have taken the measurements and fitted the BET equation to the isotherm data at 0°C, −10°C, −20.7 and −33.6°C for relative pressures less than 0.3. In performing the fit we recognise that when the heat of adsorption (ΔH) is constant, the isotherm parameter at one temperature ($c_{BET}^{T_1}$) will be related to that at another temperature ($c_{BET}^{T_2}$) through the relation,

$$\frac{C_{\mathrm{BET}}^{T_1}}{C_{\mathrm{BET}}^{T_2}} = \exp\left[\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \tag{12}$$

Table 3 contains the results of the fit with the magnitude of the value for the heat of adsorption (ΔH) being 19 kJ/mol and the saturation capacity ($C_{\mu \mathrm{s}}$) being 6.1 mmol/cm^3.

The value for the saturation capacity and heat of adsorption for SO_2 obtained from the data agrees well with the

Table 2
Properties of Carbolac I pellet

Material	Porosity $y(\varepsilon)$	Helium density (g/c.c.)	Cross-sectional area (cm^2)	Pellet length (L, cm)
Carbolac I	0.5	2.12	0.07	0.91

Table 3
Parameters obtained from the fit of the BET equation to the SO_2 data

Isotherm parameter	0°C	−10°C	−20.7°C	−33.6°C
C_{BET}	12	20	28	40

Table 4
Parameters obtained from the fit of Eqs. (11a) and (11b) to the time lag for SO_2 at four temperatures

Diffusion parameter	0°C	−10°C	−20.7°C	−33.6°C
D_e (cm^2/s)	2.4×10^{-3}	2.3×10^{-3}	2.2×10^{-3}	2.1×10^{-3}
α	0.05	0.05	0.05	0.05
$D_{\mu 0}$ (cm^2/s)	1.6×10^{-5}	1.5×10^{-5}	1.1×10^{-5}	7.5×10^{-6}

value obtained for CO_2 upon the same material as is calculated by [5].

Having evaluated the isotherm parameters and noting that the helium permeation experiment has provided the effective diffusivity of the gas phase (presented in Table 4), it is possible to now predict the time lag for a given upstream concentration. The measured values of the time lag for the given upstream concentration are plotted in Fig. 1 and shown as open circles. The fit of Eqs. (11a) and (11b) is also shown on the same plot. The fit is obtained by error minimisation with the restriction that the surface diffusivity at zero loading obtained for one temperature ($D_{\mu 0}^{T_1}$) will be related to that at another temperature ($D_{\mu 0}^{T_2}$) through the relation,

$$\frac{D_{\mu 0}^{T_1}}{D_{\mu 0}^{T_2}} = \exp\left[\frac{-E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{13}$$

where E is the activation energy for the surface diffusion. It can be seen that the fit is very good in predicting the relationship. The values of the parameters obtained from the fit are presented in Table 4 with the value for the activation energy (E) being 14 kJ/mol. The ratio of the activation energy for surface diffusion to the heat of adsorption is 0.74.

In the application of Eq. (6), [5] have used the parameter α simply as a fitting parameter because the literature data does not contain information regarding mobility at high loading where liquid surface is approached. The same applies to the data used in this paper, hence we also use α as a fitting parameter. However, here we treat the parameter as a constant (independent of temperature) to increase the significance of the minimisation result.

Chen and Yang [5] have evaluated the relevant dynamic parameters for CO_2 diffusion on Carbolac I from data obtained from a permeability experiment. The surface diffusivity at zero loading is smaller for SO_2 and the activation energy for surface diffusion larger due to the differing potential interactions of the molecules with the solid. However, both are in the same order of magnitude as is the parameter α, which is within an acceptable range [5]. This result not only provides validation for the model proposed by [5] but more importantly for experimenters verifies that measurement of the time lag provided useful means for characterisation of the permeation process.

Fig. 2 presents the dependence, as predicted by Eq. (6), of the adsorbed phase diffusivity for SO_2 permeation (at three temperatures) upon surface coverage. As discussed earlier, the mobility increases to a maximum at monolayer coverage, then decreases as loading increases. Relating this result to the classification scheme proposed by [5], SO_2 permeation can be placed into the Type III category typical of multilayer surface diffusion.

In order to give an indication of the concentration profile along the pellet, we have plotted the profile for

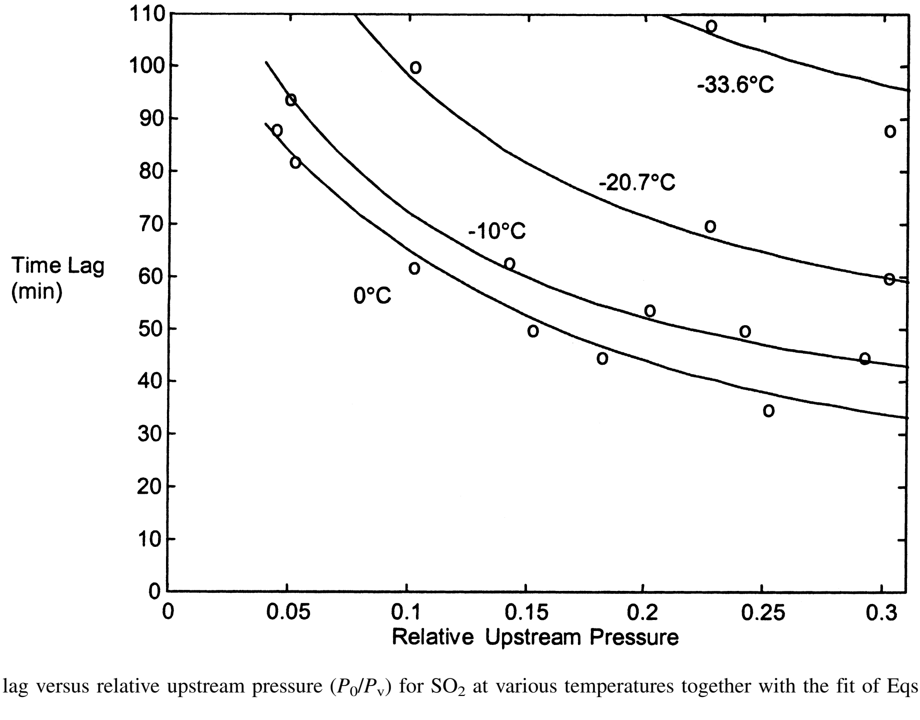

Fig. 1. The time lag versus relative upstream pressure (P_0/P_v) for SO_2 at various temperatures together with the fit of Eqs. (11a) and (11b).

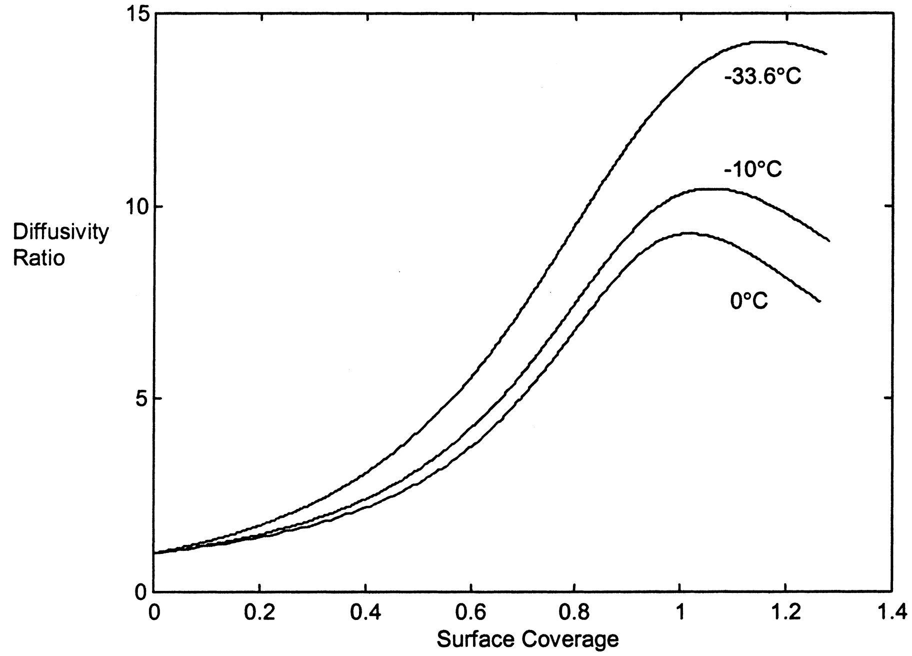

Fig. 2. Dependence of the adsorbed phase diffusivity ratio ($D_\mu/D_{\mu0}$) upon surface coverage (θ).

SO_2 permeation at −33.6°C, for the upstream pressures indicated on Fig. 3. We obtain the profile from numerical evaluation of Eqs. (8) and (9). The plot shows that at higher relative pressures the profile is non-linear because of the non-linear adsorption and surface diffusion process. At very low upstream concentration, the profile becomes linear as a result of concentration independent diffusivity.

2. Conclusions

The dependence of the adsorbed phase mobility upon the concentration of the adsorbed phase at concentrations higher than monolayer coverage but still within the BET limitations can be described well by the model proposed by [5]. Experimental determination of this dependence can be undertaken by various means but here we have shown that

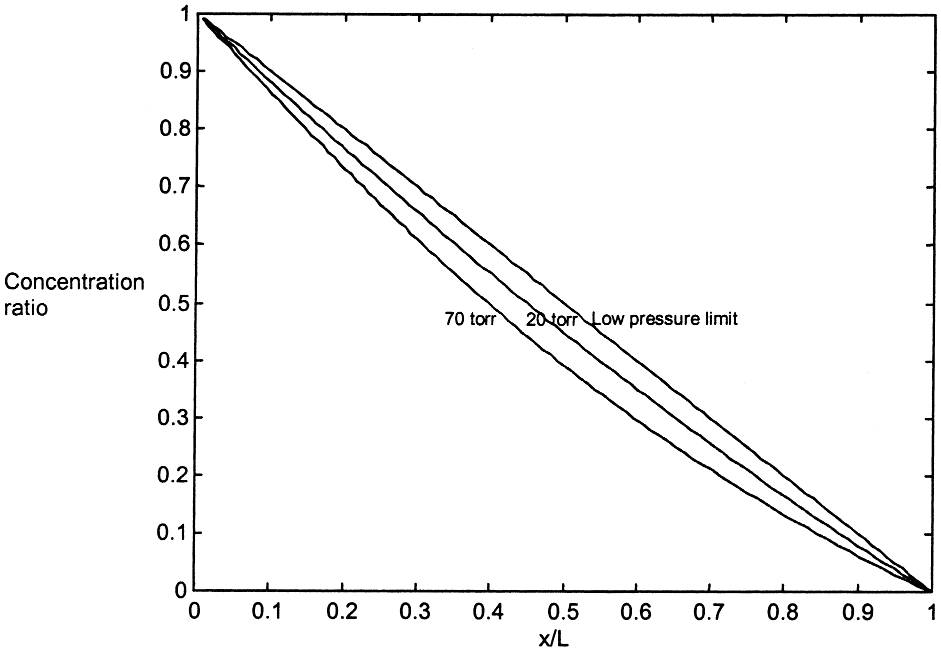

Fig. 3. Plot of the concentration ratio (C/C_0) versus the non-dimensional position along the pellet, for the upstream pressures indicated.

measurement of the time lag for diffusion can provide a reliable and accurate means for experimentation.

3. Nomenclature

A	cross-sectional area of medium
C	concentration of diffusing species
C_V	is equal to PV/(RT)
$C_{\mu s}$	saturation capacity
C_0	upstream concentration
c_{BET}	BET isotherm parameter
D	diffusivity
D_e	effective diffusivity of the gas phase
$D_{\mu 0}$	adsorbed phase diffusivity at zero loading
E	activation energy for adsorbed phase diffusion
J	flux
H	parameter defined by Eq. (3)
L	length of the pellet
N	parameter defined by Eq. (7)
P	pressure
P_V	vapour pressure
R	gas constant
T	absolute temperature
t	time
t_{lag}	time lag
V	volume of vessel in which measurement takes place
x	displacement in the direction of diffusion
ΔH	heat of adsorption
α	diffusion parameter defined in Eq. (6)
ϕ	parameter defined in Table 1
η	parameter defined in Table 1
κ	parameter defined in Table 1
λ	parameter defined in Table 1
θ	surface coverage
ε	volume fraction

Subscripts

0	upstream
μy	adsorbed phase

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