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A FREE BOUNDARY MODEL APPLIED TO THE ESTIMATION OF THE DIFFUSION COEFFICIENT IN A GAS-SOLID SYSTEM

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ABSTRACT

A practical approach consisting in the combination of analytical arguments, based on a free boundary model, and experimental data in order to estimate the diffusion coefficient in a gas-solid system is presented.

Gas-solid systems constitute by polyethylene–i-butane and polyethylene–n-butane have been used for the prediction of the diffusivity.

The values which were obtained by the present approach exhibit a good agreement with those calculated from the permeation coefficient.

1. INTRODUCTION

Looking for a competitive separation process like as the permeation, the development and optimal choice of membrane materials become necessary. On this subject, equations modelling the permeation process are required. The parameters contained in such a model must be obtained from simple experiments. The knowledge of solubility and diffusivities are very important to solve the separation problem.

Two groups of experimental techniques have been proposed for the estimation of the diffusion coefficient [5] One group uses stationary techniques the other one uses unsteady techniques. For the first group, the advantage and disavantage are the simplicity of the mathematical models and the difficult experimentation respectively. While for the gravimetric technique (the second group) [4], they are, accuracy in experimental data and the difficult in the mathematical treatment respectively. In this paper we try to get the advantages of both techniques.

2. EXPERIMENTAL

Unsteady state experiments to estimate the mean value of the diffusivity coefficient were carried out in a CAHN-RG high-vacuum electrobalance. The temperature range investigated was −15 to 40 ^{o}C where as that of pressure was up to 600 mmHg. A DOW 123 polyethylene membrane with following properties : density 0.9157 gr/cm^3 at 30^{o}C, determined by ASTM 792−66; thickness 25 μm; volume fraction of the amorphous phase 0.57 cm^3 (amorphous)/cm^3 (polymer) at 30 ^{o}C; number average molecular weight 161,000 g/mol. I-butane and n-butane gases were used. Using unsteady gravimetric technique, described in [3], films samples were subject to vacuum (10^{-4} mmHg) in the thermobalance arm until their weight achieved a constant value. The arm region where the samples lied was immersed into a thermostatic bath at specific temperature which was registered. Once uniform temperature condition were met, a given amount of vapor was admitted in the system and the weight variation as a function of the time was recorded. This procedure has been repeated until the maximum allowed value of the pressure was reached ensuring that no vapor condensation takes place

3. ANALYTICAL MODEL

Let us consider a polymeric membrane swelling for a hydrocarbon solution. The following assumption are considered : Once the gaseous component reachs a threshold concentration on the gas-polymer interface, it diffuses through the membrane in the x direction being immobilized by a quickly and irreversible transformation. Then a swelling front is generated whose position is given by the free boundary $x = s(t)$, $t>0$ where the initial condition $s(0)= 0$ is satisfied. Moreover, the hydrocarbon diffusion coefficient D in the satured or swollen region of the polymer is considered a constant for each experimental condition. The process is described in Fig. 1 .

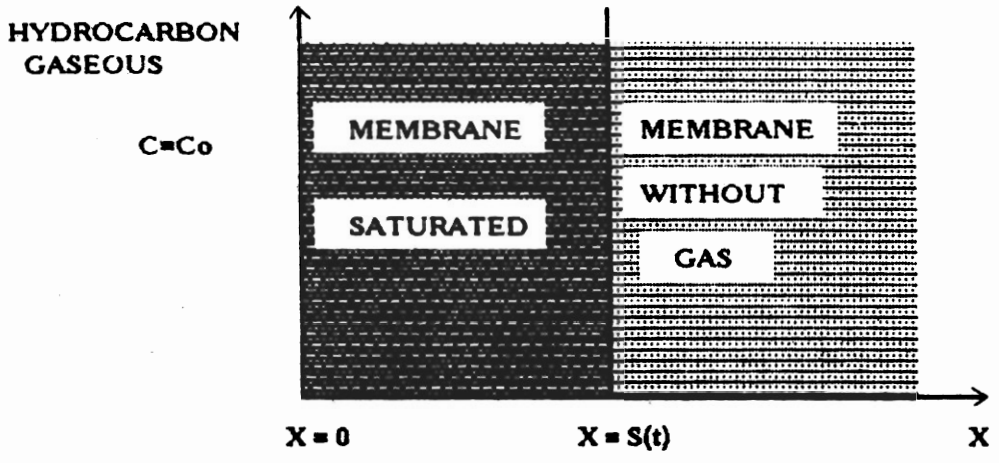

FIG. 1

4. MODEL EQUATIONS

A free boundary model [1, 2, 5, 6] with an overspecified condition for the unidimensional diffusion equation under the preceding assumptions is given [8, 9,10]:

(1) $D\, c_{xx} - c_t = 0\,, \quad 0 < x < s(t)\,, \quad t > 0\,,$

(2) $c(0, t) = C_0\,, \quad t > 0\,,$

(3) $A \int_0^t D\, c_x(0,\tau)\, d\tau = -\alpha \sqrt{t}\,, \quad t > 0\,,$

(4) $c(s(t), t) = 0\,, \quad t > 0\,,$

(5) $D\, c_x(s(t), t) = -\beta\, \dot{s}(t)\,, \quad t > 0\,,$

(6) $s(0) = 0\,,$

where $c = c(x,t)$ denotes the concentration profile of the hydrocarbon in the swollen area; $s(t)$ gives the position at time t of the moving interface and separates the two regions in the membrane, the saturated and unsaturated one, $s(t)$ is a free boundary because it is a priori an unknown; D is the unknown diffusion coefficient in the system; C_0 , α and β are positive parameters and A a positive constant, which is a experimental data. In [11], some free boundary problems were considered for reaction-diffusion system.

The equation (3) gives a overcondition on the fixed boundary $x = 0$ of the membrane [1, 8]; such a condition plays an important role in the estimation of the

coefficient D in this paper.

The coefficients A and α denote the cross section of the membrane and the initial slope of the experimental curve relating the total mass of the gas absorbed as a function of the square root of time. Let p_{i-1} , p_i , p_{i+1} denote a level pressure in a former, actual and posterior step in the experimental; C_0 is taken as the difference between the equilibrium concentrations at the pressure p_{i+1} and p_i ; parameter β can be interpreted as a property of the membrane determinated by the progresive swelling during the process. The modification of this property can be assimilate to the differences of concentrations at the former step at which the experimental is carried out. In view of the last consideration, the parameter β is calculate as the difference between the equilibrium concentrations at the pressures p_i and p_{i-1} .

The concentration profile and the free boundary position, for problem (1)–(6), are described by

$$c(x,t) = C_0 - \frac{C_0}{\operatorname{erf}\left(\frac{\sigma}{\sqrt{D}}\right)} \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \quad 0 < x < s(t), \quad t > 0, \tag{7}$$

$$s(t) = 2\,\sigma\,\sqrt{t}, \quad t > 0, \quad \text{with } \sigma > 0, \tag{8}$$

where erf is the error function, defined by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\, dt \ , \tag{9}$$

The coefficients $D > 0$ and $\sigma > 0$ must be determined in such a way that Eqs. (7) and (8) satisfy (3) and (5). So that, the following system of two unknowns is obtained :

$$\operatorname{erf}\left(\frac{\sigma}{\sqrt{D}}\right) = \frac{2\,A\,C_0\,\sqrt{D}}{\alpha\,\sqrt{\pi}}, \tag{10}$$

$$\frac{\sigma}{\sqrt{D}}\ \operatorname{erf}\left(\frac{\sigma}{\sqrt{D}}\right) \exp\left(\frac{\sigma^2}{D}\right) = \frac{C_0}{\beta\,\sqrt{\pi}}\,. \tag{11}$$

In term of the dimensionless variable ξ , defined by :

$$\xi = \frac{\sigma}{\sqrt{D}} > 0\,, \tag{12}$$

the non-linear system (10)–(11) can be written as follows :

$$\text{(13)} \qquad \operatorname{erf}(\xi) = \frac{2\,A\,C_0\,\sqrt{D}}{\alpha\,\sqrt{\pi}}\,,$$

$$\text{(14)} \qquad \xi\ \operatorname{erf}(\xi)\,\exp(\xi) = \frac{C_0}{\beta\,\sqrt{\pi}}\,.$$

We remark that equation (14) has a unique solution (called ξ_0) for any data. Then, from (12) and (13) the expression for D and σ are obtained as follows (called D_0 and σ_0):

$$\text{(15)} \qquad D_0 = \frac{\pi\,\alpha^2}{4\,A^2\,C_0^{\,2}}\,\operatorname{erf}^2(\xi_0) = \frac{\alpha^2}{4\,A^2\,\beta^2}\ \frac{\exp\left(-2\,\xi_0^{\,2}\right)}{\xi_0^{\,2}}\,,$$

$$\text{(16)} \qquad \sigma_0 = \frac{\alpha\,\sqrt{\pi}}{2\,A\,C_0}\ \xi_0\,\operatorname{erf}(\xi_0) = \frac{\alpha}{2\,A\,\beta}\,\exp\left(-\xi_0^{\,2}\right).$$

REMARK

The methodology used in this paper is a variant of those developed in [8, 9, 10] for the determination of thermal coefficients for a semi-infinite material through a phase-change process.

5. RESULTS

In Table 1 diffusion coefficient values from another method [7] and from Eq.(15) for i-butane–polyethylene, and n-butane–polyethylene systems in a usefull experimental range are illustred.

A good agreement is shown between the free boundary model and the values from permeation coefficient.

The differences between average diffusion coefficient results could be explained due to the different pressure conditions under which both methods were performed. In fact, it should be noticed that the results obtained by the stationary technique have to be extrapolated to the operating condition of the unsteady state experiments.

TABLE 1

T °C	P(mmHg)	DIFFUSION (cm^2/s)	
		Dfm	Dper[7]
I-BUTANE POLYETHYLENE e=2.5E^{-3} cm			
-15	398	$0.193 \cdot 10^{-7}$	$0.15 \cdot 10^{-7}$
	632	$0.497 \cdot 10^{-7}$	$1.78 \cdot 10^{-7}$
0	387	$0.539 \cdot 10^{-7}$	$0.88 \cdot 10^{-7}$
15	502	$0.925 \cdot 10^{-7}$	$1.47 \cdot 10^{-7}$
	654	$1.905 \cdot 10^{-7}$	$3.60 \cdot 10^{-7}$
30	280	$0.883 \cdot 10^{-8}$	$1.15 \cdot 10^{-8}$
	383.5	$1.196 \cdot 10^{-8}$	$2.25 \cdot 10^{-8}$
N-BUTANE POLYETHYLENE e=2.5E^{-3} cm			
0	165	$1.256 \cdot 10^{-7}$	$0.62 \cdot 10^{-7}$
	272	$2.146 \cdot 10^{-7}$	$1.08 \cdot 10^{-7}$
10	206	$0.657 \cdot 10^{-8}$	$0.33 \cdot 10^{-8}$
	316	$0.988 \cdot 10^{-8}$	$0.53 \cdot 10^{-8}$
	422	$0.667 \cdot 10^{-8}$	$0.74 \cdot 10^{-8}$
	536	$1.238 \cdot 10^{-8}$	$1.20 \cdot 10^{-8}$
	660	$1.938 \cdot 10^{-8}$	$2.15 \cdot 10^{-8}$
20	215	$0.624 \cdot 10^{-8}$	$0.88 \cdot 10^{-8}$
	322	$1.184 \cdot 10^{-8}$	$1.38 \cdot 10^{-8}$
	438	$1.458 \cdot 10^{-8}$	$2.18 \cdot 10^{-8}$
	546	$2.278 \cdot 10^{-8}$	$3.40 \cdot 10^{-8}$
40	222	$0.386 \cdot 10^{-7}$	$0.67 \cdot 10^{-7}$
	333.5	$0.712 \cdot 10^{-7}$	$0.98 \cdot 10^{-7}$

6. CONCLUSIONS

* The considered assumptions describe the system and the physical phenomena satisfactorily.

* The approximation based in the free boundary model allows to develop a simple model for the diffusion coefficient calculation.

* The free boundary model gets the advantages of the stationary and unsteady techniques, the simplicity of the mathematical models and accuracy in experimental data.

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NOMENCLATURE

A	cross section of the membrane
c	hydrocarbon concentration
C_0	Boundary concentration
D	hydrocarbon diffusion coefficient
erf	error function
p	pressure
s(t)	position at time t of the moving interface
t	time variable
x	spatial

Greek Symbols

α	slope of the experimental curve mass vs $\sqrt{t}$
β	difference between two equilibrium concentrations
σ	coefficient which characterizes the boundary s by Eq. (8)
ξ	dimensionless parameter defined by Eq. (12)
ξ_0	unique positive solution of the Eq. (14).

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