Study of Sorption Processes in Cigarette Filter Materials*

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INTRODUCTION

Adsorption and desorption processes are of interest in many diverse areas such as pollution control, gas chromatography and cigarette filtration. We have developed a versatile method for studying sorption processes in porous materials which is basically a modification of frontal chromatography. A fixed bed of the porous adsorbent is challenged with a steady flow of carrier gas and vapors. The effluent gas is analyzed at periodic intervals by seizing small samples and automatically injecting them into a gas chromatograph. When compared to frontal chromatography there are two key advantages to this system: [1] the detection system is independent of flow rate through the fixed bed adsorber, and [2] the system is readily adaptable to mixtures.

The system has given excellent results for the case of cigarette filters and pure nicotine vapor. Data obtained from this work has been fit to a published mathematical model (1) that was originally derived for chemical engineering unit processes. Key assumptions in this model were [1] reversible adsorption, [2] linear isotherm, and [3] first order kinetics. The mathematical model

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contains two parameters which can be adjusted to give the best fit to experimental data. The parameters are directly related by theory to 1. the equilibrium partition coefficients for the adsorbed and vapor states, and 2. the observed rate constants for the adsorption and desorption steps. Thus, the experimental method and model combine to give an excellent general method for the study of adsorption and desorption kinetics in packed beds.

EXPERIMENTAL

A schematic of the experimental apparatus is shown in Figure 1. The main functions of the apparatus are: [1] inert diluent gas generation, [2] vapor generation, [3] filtration, [4] effluent gas sampling, and [5] analysis of effluent gas sample.

For the experiments reported in this paper, the inert diluent gas was Union Carbide UltraHigh Purity grade nitrogen and the vapor was nicotine obtained from Eastman Chemicals.

The nicotine vapor was generated by passing the nitrogen gas from cylinder 1 through a 250 cm^3 round bottom flask containing 10 cm³ of nicotine which was agitated with a magnetic stirrer to enhance vaporization. The output of the vapor generation flask was con-





trolled at the outlet with a Gilmont Capillary-Metering valve. The pressure in the generation flask was usually 300-400 mm Hg above atmospheric pressure.

It was determined that the nicotine concentration was independent of the nitrogen flow rate through the flask over the flow rate range of 300-1200 cm³/min used in these experiments. Therefore it was possible to obtain data at different flow rates which was not confounded by concentration differences. These experiments were done at near nicotine saturation and the diluent from nitrogen source number 2 was not used; however, in future experiments the concentration can be kept constant at lower levels and at different flow rates through the filter by proper balancing of nitrogen flow from the sources.

The filtration section was two "O"-ring seals, a rubber

Figure 3. Fraction of nicotine vapor penetrating cellulose acetate filter versus time.



dental dam, and the filter. The filter was placed in the dam and clamped between the two "O"-ring seals.

The effluent from the filter passed through the Union Carbide sliding plate valve fitted with a 1.4 cm³ sampling loop. The valve was timed to operate at fixed intervals to transfer a sample to the Bendix 2600 gas chromatograph for analysis. The sampling rate depended upon the analysis rate. In these experiments the sampling rate was one and two minutes. Figure 2 is an example of the recorder output. The connection dead volume was negligible compared to volume flow between samples. The 0.8 meter column contained $8^{\circ}/_{\circ}$ Apiezon-L on 60×80 mesh Chrom-G. Flame ionization was used for detection.

The intermittent sampling technique was incorporated to handle multiple vapor analysis in future experiments and to ascertain sample purity in single vapor experiments. Passing the effluent directly into the gas chromatograph would not allow separation into components in these experiments.

The filters were 20 mm lengths of 8 denier per filament/ 40000 total denier cellulose acetate (without additives) and paper (without additives).

RESULTS AND DISCUSSION

The results of the experiments are shown in graphical form in Figures 3 and 4 where the fraction penetrating is plotted versus time. The time required for nicotine vapor to breakthrough decreases as the total gas flow rate increases. Knowing the total gas flow rate, inlet





Figure 5. Amount of nicotine vapor accumulated on cellulose acetate filter versus time.



nicotine concentration, and breakthrough curve one can calculate the amount of nicotine accumulated on the filter as a function of time:

$$M = Q C_o \int_o^t (1 - \frac{C}{C_o}) dt \qquad [1]$$

where

- M =amount accumulated on filter (g),
- C_0 = nicotine vapor concentration at inlet (g/cm³),
- C = nicotine vapor concentration at exit at time t (g/cm^3) ,

t = time(s),

Q = total volumetric gas flow rate (cm³/s).

The total gas flow rate was assumed constant through the filter since the pressure drop $(1^{"} H_2O)$ across the filter was insignificant compared to the head pressure of 1 atmosphere at the highest flow rate used.

The absolute amount of nicotine accumulated on the filter was calculated using equation 1 for each flow rate and the results are shown in Figures 5 and 6 for cellulose acetate and paper adsorbents. In both cases the curves converge at long times which indicates that equilibrium can be attained at all of the flow rates studied. The total amount accumulated on the filter at equilibrium should only depend on the inlet concentration of the vapor and the adsorbent (filter).

Since equilibrium is attainable, it is possible to calculate an equilibrium partition coefficient for nicotine vapor (in N_2) in cellulose acetate and paper:

$$K = \frac{C_0}{\varrho_G S_{\infty}} = \frac{C_0 W_F}{\varrho_G M_{\infty}}$$
[2]

where

- S_{∞} = amount of adsorbate accumulated on filter at equilibrium, (C = C₀), per unit weight of filter, ϱ_{G} = density of diluent gas (g/cm³),
- W_F = weight of filter (clean) (g).

Figure 6. Amount of nicotine vapor accumulated on paper filter versus time.



In practice, $100^{0}/_{0}$ penetration (C = C₀) was not reached, however, values upwards of $90^{0}/_{0}$ were obtained and the following approximation was used.

$$K \simeq \frac{\Phi_t C_o W_F}{\varrho_G M_t}$$
 [3]

where

- Φ_t = fraction penetrating filter at some time, t, near equilibrium = $(C/C_0)_t$,
- M_t = amount accumulated on filter at time corresponding to that at which Φ_t is measured.

Figure 7. Log of percent of nicotine vapor penetrating cellulose acetate filter versus filter length.



 Table 1.
 Comparison of partition coefficients at various carrier gas flow rates: Cellulose acetate.

Nicotine vapor	on untreated 20 (8/40,000) filte	mm cellulose acetate rs		
Flow rate (cm³/min)	Partition coefficients (a)			
	Model (b)	Experimental (c)		
300	.042	.038		
600	.036	.045		
1200	.036	.041		
	Average .038	Average .041		

(a) Units are: (g nicotine / g nitrogen) / (g nicotine / g filter).

(b) Calculated from equation 8 (model).

(c) Calculated from amount accumulated versus effluent concentration (experimental), equation 3.

Equation 3 was found to be valid by testing with several values of $(C/C_0)_t$ and M_t corresponding to $(C/C_0)_t > 0.8$; K was constant. The partition coefficients for nicotine in untreated cellulose acetate and paper systems are given in Tables 1 and 2. According to the definition for K, nicotine has a higher affinity for cellulose acetate than paper. As expected, the tables show K to be nearly independent of flow rate.

We have shown experimentally that nicotine adsorption is reversible. Furthermore, as Figure 7 shows, the amount removed is a function of filter length. Thus, the model to describe the sorption processes in these systems must be a function of exposure time, filter length and contain a reversible kinetic mechanism.

The Hougen-Marshall (1) model for fixed bed adsorption fits the nicotine-cellulose acetate and nicotine-paper systems quite well. The assumptions for their model were:

a. Steady flow process; constant flow rate.

- b. Rate controlling process is first order, reversible.
- c. Volume of the bed is small compared to the volume of gas passing through it.
- d. Ideal gas behavior; Dalton's law holds.
- e. Linear adsorption isotherm.
- f. Inlet concentration of vapor is constant.
- g. Amount of adsorbate on filter at t=0 is zero.
- h. Lateral diffusion minimal due to residence times used in experiments.

The expanded Hougen-Marshall solutions to the continuity equations for gas-phase and solid-phase including the above assumptions are given by equations 4 and 5.

$$C/C_{o} = e^{-(bt+ax)} \sum_{i=0}^{\infty} \frac{(bt)^{i}}{i!} \sum_{R=0}^{i} \frac{(ax)^{(i-R)}}{(i-R)!}$$
[4]

$$S/S_{\infty} = e^{-(bt + ax)} \sum_{i=0}^{\infty} \frac{(ax)^{i}}{i!} \sum_{R=0}^{i} \frac{(bt)^{(i-R)}}{(i-R)!} -1$$
 [5]

where

- x = bed length (cm),
- t = exposure time (s),
- a = bed length parameter, reciprocal length (cm⁻¹),
- b = exposure time parameter, reciprocal time (s⁻¹).

 Table 2.
 Comparison of partition coefficients at various carrier gas flow rates: Paper.

Flow rate	Partition coefficients (a)		
(cm³/min)	Model (b)	Experimental (c)	
300	.103	.098	
600	.100	.088	
1200	.098	.089	

(a) Units are: (g nicotine / g nitrogen) / (g nicotine / g filter).

(b) Calculated from equation 8 (model).

(c) Calculated from amount accumulated versus effluent concentration (experimental), equation 3.

Equation 4 was applied to the systems reported here and best fit values of a and b were obtained at each flow rate. These values are given in Table 3 which shows that a decreases with an increase in flow rate and that b is independent of flow rate.

The internal consistency of a and b may be checked in two ways: [a] compare C/C_0 calculated from the best fit to the experimental C/C_0 as in Figures 3 and 4, and [b] determine if calculated values of a and b are consistent with relationships from the model.

The calculated values of C/C_0 agree with experimental values in most cases except at the longer times at the lowest flow rate in the nicotine cellulose acetate system. This could be caused by a competitive process such as absorption requiring long times and low flow rates. The fact that this does not occur for the same conditions in the nicotine-paper system could be explained by the greater affinity of nicotine for cellulose acetate.

There are three mathematical relationships from the *Hougen-Marshall* model which can be used to check the internal consistency of a and b. These are:

$$a = \frac{k_0 a_v P M_G}{G}$$
 [6]

$$b = \frac{K k_0 a_v P M_G}{\varrho_F}$$
 [7]

$$K = \frac{b}{a} \frac{\varrho_F}{G}$$
[8]

where

 $k_o = observed$ forward rate constant,

 $a_v = external surface area of bed per unit volume of bed (cm²/cm³),$

P = absolute pressure in bed (mm),

 $M_Q =$ gram molecular weight of diluent gas,

G = mass flux of diluent gas (based on crosssectional area of bed) (g/cm²/s),

 ρ_F = density of bed (g/cm³).

Thus, if one plots log (1/a) versus log (G) and assumes all other quantities in equation 6 are constant, a straight line with a slope of 1.0 should be obtained. The plots in Figure 8 have slopes of 0.9 and 0.96 for the cellulose acetate and paper systems respectively.

 Table 3.
 Variation of parameters with carrier gas flow rate.

Flow rate (cm³/min)	Adsorbent	a (cm ⁻¹)	b (sec ⁻¹)
300	Cellulose acetate	3.44	0.018
800	Collulono costato	4.00	0.033
600	Paper	3.12	0.021
1200	Cellulose acetate	1.00	0.018
	Paper	1.20	0.031

Equation 7 indicates that b should be independent of the diluent mass flux. This appears to be confirmed by the calculated values of b in Table 3.

The relationship given in equation 8 allows one to calculate the equilibrium partition coefficient from the parameters a, b, G, and ϱ_F . Comparison of the value of K calculated from equation 8 with that calculated from the raw data with equation 3, as shown in Tables 1 and 2, is the third internal consistency test. There is excellent agreement in both systems.

Figure 8. Plot of reciprocal length parameter versus nitrogen mass flux.



CONCLUSIONS

We have shown that nicotine vapor adsorption in cellulose acetate and paper filters is a reversible process

with a finite equilibrium partition coefficient, and that the process may be described by the *Hougen-Marshall* fixed bed adsorption model.

SUMMARY

A method for studying adsorption-desorption kinetics in porous materials is described.

A fixed bed of the adsorbent is challenged with a constant concentration of vapor in an inert carrier and the effluent vapor concentration is monitored as a function of time by using a gas chromatograph. Results obtained with commercial filters and nicotine vapor are reported. They fit a mathematical model based on a first-order, reversible rate-controlling process and a linear adsorption isotherm.

ZUSAMMENFASSUNG

Es wird eine Methode zur Untersuchung der Kinetik von Adsorptions- und Desorptionsvorgängen in porösen Stoffen beschrieben.

Eine feste Schicht des Adsorbens wird einem Dampf konstanter Konzentration in einem inerten Träger ausgesetzt und die Konzentration des austretenden Dampfes unter Benutzung eines Gaschromatographen in Abhängigkeit von der Zeit untersucht. Über die mit handelsüblichen Filtern und Nikotindampf erzielten Ergebnisse wird berichtet. Diese entsprechen einem mathematischen Modell, das auf einer linearen Adsorptionsisotherme und einem reversiblen geschwindigkeitsbestimmenden Prozeß erster Ordnung basiert.

RESUME

On décrit une méthode pour l'étude de la cinétique des phénomènes d'adsorption/désorption sur matériaux poreux.

Une couche fixe d'adsorbant est maintenue en contact avec une concentration constante de vapeur dans un vecteur inerte. La concentration de la vapeur effluente est mesurée en fonction du temps par un chromatographe en phase gazeuse. On présente les résultats obtenus avec des filtres commerciaux et de la vapeur de nicotine. Ils correspondent à un modèle mathématique basé sur une isotherme linéaire d'adsorption et sur une réaction réversible du premier ordre déterminant la vitesse du processus en question.

REFERENCES

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