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STUDY OF FRONTAL ANALYSIS BY CHARACTERISTIC POINT

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SUMMARY

An analytical solution is derived for the desorption of an adsorbate that obeys a Langmuir isotherm and diffuses at a finite rate. The solution is integrated to give the adsorption isotherm by the technique of frontal analysis by characteristic point. The results indicate that the integration procedure does not yield the real isotherm for a system with a finite diffusion rate. The ratio of the equilibrium speed to the elution speed is given as a criterion for deviation from the real isotherm. An experimental result is given to show the deviation of the measurement of the adsorption isotherm of ethane on activated carbon.

INTRODUCTION

The method of frontal analysis by characteristic point (FACP) was introduced by Wilson¹, Weiss², deVault³ and Glueckauf⁴ for determining adsorption isotherms. This technique applies to the diffuse side of the concentration profile. In gas–solid chromatography (GSC) systems with a Langmuir isotherm, the desorption part of the chromatogram is a diffuse boundary. A diffuse boundary occurs also at the front for an anti-Langmuir or type III BET isotherm. For either case, the solid-phase concentration q is given by the following integral expression:

$$(1 - \varepsilon) q = \frac{\varepsilon u}{L} \int_0^c t_R dc \quad (1)$$

where u is the interstitial flow-rate of gas mixture, L is the column length, t_R is the net retention time measured at concentration c , and ε is the void fraction of the chromatographic column. The adsorption isotherm is obtained from a single chromatogram.

Experimental work with a step change in concentration was carried out by Gregg and Stock⁵ who measured the adsorption isotherms of four hydrocarbons on silica gels, block-dried calcium carbonate and calcium sulphate. They observed all five types of BET isotherms. Instead of using a step change or a rectangular input, a large sample pulse injected by a syringe can usually achieve a diffuse boundary because both adsorption and desorption phenomena occur, and one of them must be a

diffuse boundary. A pulse-flow technique was applied by Huber and Keulemans⁶ to measure the adsorption isotherm of ethylene on active charcoal, and by Gray and Guillet⁷ to measure the adsorption isotherm of *n*-decane and 1-hexanol on polystyrene and poly(methyl methacrylate). Even though the isotherms measured by the static method and the chromatographic method agree^{5,6,8-10}, we observed experimentally that the adsorption isotherm of ethane on activated carbon measured by the FACP method usually has a higher curvature compared to the true isotherm.

Huber and Keulemans⁶ gave six assumptions for deriving eqn. 1. One of them is the equilibrium between gas and solid phases; however, this equilibrium is not always attained, particularly for large adsorbent granules with very small pore size. A criterion is needed to know under what conditions one can accept the adsorption isotherm calculated on the basis of eqn. 1. In this paper, we present a theoretical discussion for a non-equilibrium Langmuir system by comparing the integration of the analytical solution derived from the assumption of finite adsorption/desorption speed. A Langmuir system is chosen in this study because the analytical solution can be derived.

SOLUTION OF DIFFERENTIAL EQUATIONS

The gas-phase concentration c and the solid-phase concentration q are related by the following equations:

$$\frac{\partial c}{\partial t} + u \cdot \frac{\partial c}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q}{\partial t} = 0 \quad (2)$$

$$\frac{\partial q}{\partial t} = k_a(q_m - q)c - k_dq \quad (3)$$

with the conditions

$$z = 0 \quad c(0, t) = 0 \quad (4)$$

$$t = 0 \quad q(z, 0) = q_0; \quad c(z, 0) = c_0 \quad (5)$$

where k_a and k_d are the adsorption and desorption rate constants, respectively, q_m is the solid-phase concentration for monolayer coverage, ε is the void fraction, and u is the linear velocity of the carrier gas. A first-order expression similar to eqn. 3 has been proposed by Glueckauf and Coates¹¹ to approximate an intraparticle diffusion. Note that at the steady state, eqn. 3 gives

$$\frac{q}{q_m} = \frac{(k_a/k_d)c}{1 + (k_a/k_d)c} \quad (6)$$

which is a Langmuir isotherm. Since the diffuse profile of a Langmuir system occurs at desorption, the initial condition, eqn. 5, is chosen as a saturated column.

Let us introduce two variables

$$x \equiv \frac{z}{u}; \quad y \equiv \left(t - \frac{z}{u} \right) \cdot \frac{\varepsilon}{1 - \varepsilon} \quad (7)$$

Then the system becomes

$$\frac{\hat{c}q}{\hat{c}y} = - \frac{\hat{c}c}{\hat{c}x} \quad (8)$$

and

$$\frac{\varepsilon}{1 - \varepsilon} \frac{\hat{c}q}{\hat{c}y} = k_a q_m c - k_a c q - k_d q \quad (9)$$

Because of eqn. 8, there exists a potential function ψ such that

$$c = \frac{\hat{c}\psi}{\hat{c}y}; \quad q = - \frac{\hat{c}\psi}{\hat{c}x} \quad (10)$$

From this definition, eqn. 9 becomes

$$\frac{\hat{c}^2\psi}{\hat{c}x\hat{c}y} + \alpha \cdot \frac{\hat{c}\psi}{\hat{c}x} + \beta \cdot \frac{\hat{c}\psi}{\hat{c}y} + \gamma \cdot \frac{\hat{c}\psi}{\hat{c}x} \cdot \frac{\hat{c}\psi}{\hat{c}y} = 0 \quad (11)$$

where $\alpha = k_d(1 - \varepsilon)/\varepsilon$, $\beta = k_a q_m(1 - \varepsilon)/\varepsilon$, and $\gamma = k_a(1 - \varepsilon)/\varepsilon$.

Eqn. 11 can be linearized by substituting^{12,13}

$$\gamma\psi = \ln f(x, y) - \beta x - \alpha y \quad (12)$$

and eqn. 11 becomes

$$\frac{\hat{c}^2 f}{\hat{c}x\hat{c}y} - \alpha\beta f = 0 \quad (13)$$

The initial conditions for eqn. 13 can be obtained from eqns. 4, 5, 8 and 12:

$$y = 0 \quad f(x, 0) = \exp [(\beta - q_0\gamma) x] \quad (14)$$

$$x = 0 \quad f(0, y) = \exp (\alpha y) \quad (15)$$

After taking the Laplace transform on x , eqn. 11 becomes

$$p \cdot \frac{\hat{c}}{\hat{c}y} \tilde{f}(p, y) - \frac{\hat{c}}{\hat{c}y} f(0, y) - \alpha\beta \tilde{f} = 0 \quad (16)$$

where p is the parameter of the Laplace operator. From eqn. 14,

$$\frac{\hat{c}}{\hat{c}y} f(0, y) = \alpha e^{\alpha y} \quad (17)$$

Eqn. 16 is a first-order inhomogeneous differential equation. The general solution is

$$\tilde{f}(p, y) = \frac{e^{zy}}{p - \beta} + De^{(\alpha\beta/p)y} \quad (18)$$

where D is the integration constant. It is determined from the relation

$$\tilde{f}(p, 0) = \frac{1}{p - (\beta - q_0\bar{\gamma})} \quad (19)$$

Eqn. 17 becomes

$$\tilde{f}(p, y) = \frac{e^{zy}}{p - \beta} + \left(\frac{p}{p - (\beta - q_0\bar{\gamma})} - 1 - \frac{\beta}{p - \beta} \right) \frac{e^{(\alpha\beta/p)y}}{p} \quad (20)$$

The inverse Laplace transform of eqn. 20 is

$$f(x, y) = e^{xy + \beta x} + \int_0^x [(\beta - q_0\bar{\gamma}) e^{-q\bar{\zeta}} - \beta] e^{\beta\bar{\zeta}} I_0 [2\sqrt{\alpha\beta y(x - \bar{\zeta})}] d\bar{\zeta} \quad (21)$$

The gas-phase concentration is determined with the aid of eqns. 10 and 12:

$$T = 1 - \frac{1}{\theta_0} + \frac{1 - \theta_0}{\theta_0} \times \left\{ \frac{1 + se^{-ws} \int_0^1 e^{s(e-1)} [(1 - \theta_0) e^{-\theta_0 se} - 1] \sqrt{\frac{1 - \varrho}{w}} \cdot I_1 [2\sqrt{ws^2(1 - \varrho)}] d\varrho}{1 + se^{-ws} \int_0^1 e^{s(e-1)} [(1 - \theta_0) e^{-\theta_0 se} - 1] I_0 [2\sqrt{ws^2(1 - \varrho)}] d\varrho} \right\} \quad (22)$$

where we define

$$T \equiv \frac{c}{c_0} \quad (23)$$

$$\theta_0 \equiv \frac{q_0}{q_m} \quad (24)$$

$$w \equiv \frac{k_d}{k_a q_m} \left(\frac{tu}{z} - 1 \right) \quad (25)$$

$$s \equiv \frac{k_a q_m z (1 - \varepsilon)}{u\varepsilon} \quad (26)$$

A similar method was applied by Thomas¹² and Zhitomirskii *et al.*¹³ to derive a solution for a step increase in the concentration. The adsorption isotherm can be integrated based on the principle of eqn. 1:

$$(1 - \varepsilon) qz = \varepsilon u \int_0^c \left(t - \frac{z}{u} \right) dc \quad (27)$$

where q is the solid-phase concentration corresponding to the gas-phase concentration c . Integrating eqn. 27 by parts and using eqns. 10 and 12, we have

$$qx = \frac{\varepsilon}{1 - \varepsilon} \cdot \left(t - \frac{z}{u} \right) c + \frac{\varepsilon}{1 - \varepsilon} \int_t^\infty c dt \quad (28a)$$

$$= yc - \frac{1}{\gamma} \cdot \ln \left\{ 1 + e^{-xy} \int_0^1 [(\beta - q_0\gamma) e^{-q_0\gamma x\varrho} - \beta] x e^{-\beta x(1-\varrho)} \times \right. \\ \left. I_0[2 \sqrt{\alpha\beta xy(1-\varrho)}] d\varrho \right\} \quad (28b)$$

Here t is the time when the gas-phase concentration at z is c . Note that eqn. 22 satisfies the mass balance equation

$$(1 - \varepsilon) q_0 z = \varepsilon u \int_{z/u}^\infty c(t, z) dt \quad (29)$$

It can be proved simply by letting $y = 0$ in eqn. 28. Eqn. 28 can be rewritten in a dimensionless form:

$$\frac{q}{q_m} \equiv \theta = \frac{w\theta_0 T}{1 - \theta_0} - \frac{1}{s} \cdot \ln \left\{ 1 + s e^{-sw} \int_0^1 e^{s(\varrho-1)} \times \right. \\ \left. \times [(1 - \theta_0) e^{-\theta_0 s \varrho} - 1] I_0[2 \sqrt{ws^2(1-\varrho)}] d\varrho \right\} \quad (30)$$

In eqns. 22 and 30, the parameter θ_0 is the fraction of the surface area covered at the beginning, and s represents the ratio between the speed of adsorption (and desorption) to the speed of the carrier gas flow. A large value of s indicates a large probability of equilibrium; therefore, it is the key parameter in our discussion.

ADSORPTION ISOTHERM

The adsorption isotherm is determined as follows. For a system with known θ_0 and s , a positive y is selected. The reduced gas-phase concentration T is calculated through eqn. 22, and the corresponding reduced solid-phase concentration θ is calculated through eqn. 30. The integrations were carried out numerically by using a polynomial approximation of the Bessel functions. When y moves from zero to infinity, an adsorption isotherm is formed. Fig. 1 shows a family of curves for $\theta_0 = 0.5$ with s as a parameter. The trend of the family of curves agrees with our expectation that an isotherm approaches the real isotherm only when the relative speed of equilibrium, *i.e.* s , is large. Note that θ is always equal to θ_0 when $T = 1$ because the integration of eqn. 28 is carried out from zero to c_0 , and the mass balance relation in eqn. 27 gives $q = q_0$.

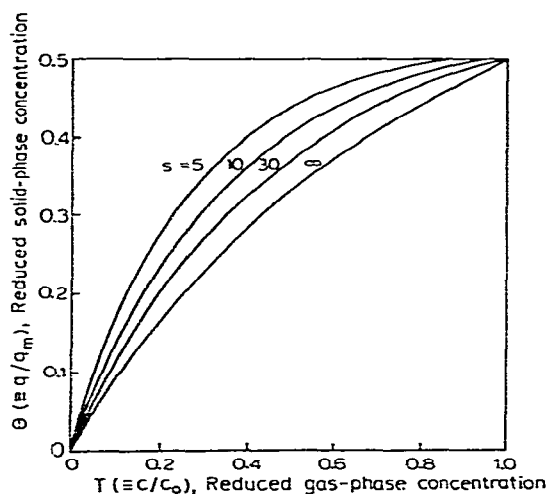


Fig. 1. Adsorption isotherms based on the frontal analysis by characteristic point technique. The parameter s is the ratio of the equilibrium speed to the elution speed. The curve for $s = \infty$ is the Langmuir isotherm. Other curves are integrated from the analytical solution of the gas-phase concentration. The solid-phase concentration is one-half of the monolayer coverage at the beginning of desorption ($\theta_0 = 0.5$).

The deviations of the calculated isotherms at finite mass-transfer speed indicate that the FACP method must be used with caution. The analytical solution¹⁴ for a linear isotherm with intraparticle diffusion indicates that a step decrease of the input concentration results in a *diffuse* desorption curve. The same mechanism can be expected to occur in other systems with non-linear isotherms; therefore, the diffusion process tends to exaggerate a diffuse chromatogram, and the adsorption isotherm obtained from the integration of eqn. 1 will have a higher curvature. This prediction can be seen easily from Fig. 1.

EXPERIMENTAL RESULTS

An experimental result for the adsorption isotherm of ethane at 25°C is given

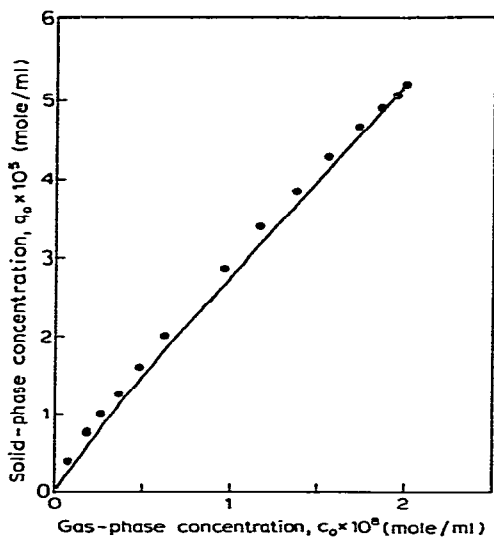


Fig. 2. Comparison of the true isotherm with the adsorption isotherm of ethane on activated carbon at 25°C measured by the FACP method. Points are values based on eqn. 28a. The solid line is a Chakravarti-Dhar type isotherm reported previously in ref. 15.

in Fig. 2. The flow system is described in a previous paper¹⁵. The experimental procedure is similar except that the column is saturated first by ethane and then a pure helium flow elutes the adsorbed ethane. The interstitial flow-rate of desorption is 8.92 cm/sec. Because the gas phase concentration c is measured at a constant interval, it is convenient to perform the integration through eqn. 28a rather than eqn. 27. This method is generally applied in the literature^{2,3}. The solid-phase concentration corresponding to each gas-phase concentration is plotted in Fig. 2. The solid line is a Chakravarti-Dhar type isotherm reported previously¹⁵. It can be seen that the FACP method gives higher solid-phase concentrations than the true isotherm. As discussed earlier, the two methods agree at the input concentration ($c_0 = 2.0 \cdot 10^{-8}$ mole/ml).

Although our primary experimental result shows a deviation as predicted, there are some differences between the two systems. For an ideal chromatography system (*i.e.* one in equilibrium without diffusion), any type of isotherm can be determined by the FACP method; therefore, it is the diffusion process that limits the use of the FACP method. The mathematical model described in eqns. 1 and 2 is a Langmuir equation without longitudinal diffusion. It predicts that a small flow-rate with large s will achieve an equilibrium measurement. The true system has both a different isotherm and longitudinal diffusion. Because of the existence of both longitudinal and intraparticle diffusion, the overall diffusion process has a minimum corresponding to the minimum in the height equivalent to a theoretical plate (HETP). A further decrease of the flow-rate below the optimal flow-rate of the HETP will increase the diffusion again; therefore, the optimal flow-rate should be chosen to measure the isotherm in the FACP method. In our previous paper¹⁵, the HETP is the key criterion that gives the asymptotic concentration profile. The HETP is the key criterion also to obtain the best measurements of the adsorption isotherm using the FACP method.

CONCLUSION

The purpose of this paper is to derive an analytical solution based on a mathematical model to demonstrate the importance of a finite diffusion rate on the determination of the adsorption isotherm by the FACP method. Our equation indicates that a single parameter s , which is the ratio of the equilibrium speed to the elution speed, can characterize equilibrium conditions. An experimental result is given to demonstrate the effect of non-equilibrium on the measurement of adsorption isotherms.

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