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DETERMINATION OF ADSORPTION EQUILIBRIUM CONSTANTS BY REVERSED-FLOW GAS CHROMATOGRAPHY

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SUMMARY

A method for determining adsorption equilibrium constants of gases or vapours between a solid adsorbent and a gas phase is described. The method is based on a technique reported earlier for measuring diffusion coefficients by reversed-flow gas chromatography. The adsorbing gas is introduced at the one end of a diffusion column, which is partly filled with the solid adsorbent, and is connected perpendicularly to an empty chromatographic column. Through the latter helium is flowing as a carrier gas, carrying over to a flame-ionization detector the solute entering at the junction of the two columns by the diffusion current. The mathematical expression describing the elution curves of the extra peaks produced because of the gas flow reversals is derived and is used to calculate the adsorption equilibrium constants of methane, ethane, *n*-butane, ethene, propene and but-1-ene between helium and aluminium oxide. From the variation of these constants with temperature, differential enthalpies and entropies of adsorption of the above gases on aluminium oxide have been calculated. They are discussed in comparison with the same parameters as determined from gas chromatographic retention data.

INTRODUCTION

In a recent paper[1], a new technique for measuring mutual diffusion coefficients in gases was reported. The method uses a short, empty chromatographic column with a gas flowing through it as a carrier gas. A small volume of another gas (solute) is introduced at the closed end of a so-called "diffusion column". This is a straight, relatively short, empty tube connected perpendicularly to the chromatographic column around its middle point. A diffusion current is established inside the diffusion column, carrying the solute gas into the stream of the carrier gas, which in turn carries the solute over to the detector. The amount of solute entering the chromatographic column by diffusion is repeatedly sampled by reversing the direction of the carrier gas flow at known times. This creates at the detector extra elution peaks by means of which the mutual diffusion coefficient of the two gases is determined.

If the diffusion column is partly filled with a porous solid adsorbent, on which the solute gas is reversibly adsorbed, the diffusion current into the carrier gas stream is delayed, and this phenomenon can be used to determine the adsorption equilibrium constant of the solute between the solid and the gas phases. It is the object of the present paper to explore this possibility.

THEORETICAL

While the carrier gas flows as shown in Fig. 1, its direction is reversed by interchanging the points D_1 and D_2 by means of a suitable valve (see Fig. 2 in ref. 1). This samples the chromatographic column and the mass of solute having entered it at $x = l'$ between $t_{tot} - t_M$ and t_M is exhibited as an extra peak "sitting" on the otherwise continuous elution curve. The flow reversal is repeated many times so as to obtain a series of extra peaks, the time elapsing between any two successive reversals being greater than the total gas hold-up time $t_M + t'_M$. The concentration–time curves at the detector are described by eqn. 30 of ref. 1:

$$c_x = c_x(l', t_{tot} - \tau)\,[u(\tau) - u(\tau - t'_M)] + c_x(l', t_{tot} + \tau)\,u(\tau) \qquad (1)$$

where

$$\tau = t - t_M, \qquad (2)$$

$c_x(l', t_{tot} - \tau)$ or $c_x(l', t_{tot} + \tau)$ is the concentration of the solute vapour in the chromatographic column at $x = l'$ and time $t_{tot} - \tau$ or $t_{tot} + \tau$, respectively, and $u(\tau)$, $u(\tau - t'_M)$ is the unit step function of argument τ and $\tau - t'_M$, respectively.

The analytical form of the function $c_x(l', t_{tot})$ is now required, and this is calculated on the following assumptions: (a) the solute is introduced in a very small

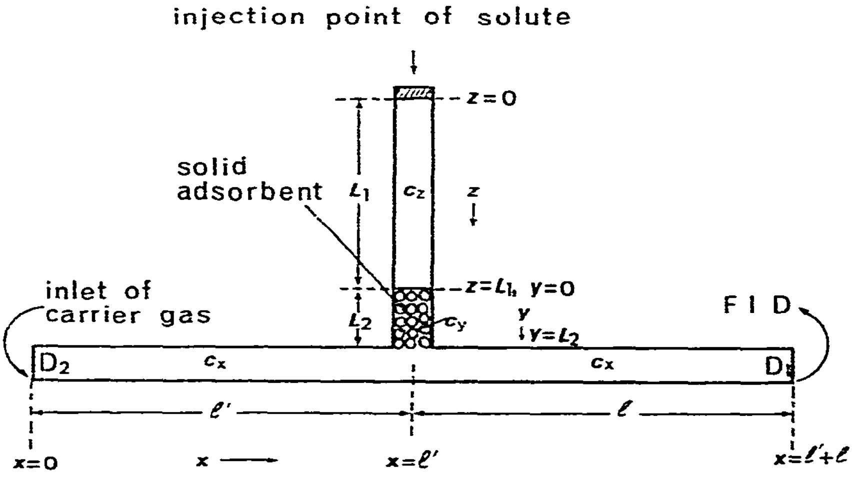

Fig. 1. Schematic representation of the diffusion ($L_1 + L_2$) and chromatographic ($l' + l$) columns for measuring partition ratios by the reversed-flow method.

section of column L_1, so that its z distribution is described by a delta function, $\delta(z)$; (b) equilibration of the solute between the gas and the solid phases in column L_2 is instantaneous; (c) the adsorption isotherm is linear. The problem will be considered separately in the two regions z and y of the diffusion column (see Fig. 1).

Region z

The concentration of the solute in this region, $c_z(z, t_{\text{tot}})$, is governed by the diffusion equation

$$\frac{\partial c_z}{\partial t_{\text{tot}}} = D_z \cdot \frac{\partial^2 c_z}{\partial z^2} \tag{3}$$

By successive Laplace transformations of this equation, first with respect to t_{tot} and initial condition $c_z(z, 0) = (m/a)\,\delta(z)$, and then with respect to z, taking the z derivative at $z = 0$ equal to zero as shown previously[1], one obtains, after taking the z inverse transform,

$$C_z = C_z(0) \cosh qz - (m/aD_z q) \sinh qz \tag{4}$$

where

$$q = (p/D_z)^{\frac{1}{2}} \tag{5}$$

and $C_z(0)$ is the t_{tot} transform of c_z at $z = 0$.

Region y

A mass balance equation for the solute in this region gives

$$\frac{\partial c_y}{\partial t_{\text{tot}}} + r \cdot \frac{\partial q_y}{\partial t_{\text{tot}}} = D_y \cdot \frac{\partial^2 c_y}{\partial y^2} \tag{6}$$

Substitution of the isotherm $q_y = Kc_y = (k/r)\, c_y$ and rearrangement leads to the modified diffusion equation

$$\frac{\partial c_y}{\partial t_{\text{tot}}} = D'_y \cdot \frac{\partial^2 c_y}{\partial y^2} \tag{7}$$

where D'_y is an effective diffusion coefficient:

$$D'_y = D_y/(1 + k) \tag{8}$$

The solution of eqn. 7, with initial condition $c_y(y, 0) = 0$, is

$$C_y = C_y(0) \cosh q'y + [C_y'(0)/q'] \sinh q'y \tag{9}$$

where

$$q' = (p/D_y')^{\frac{1}{2}} \tag{10}$$

and $C_y(0)$ and $C_y'(0)$ are the t_{tot} transform of c_y and its first y derivative, respectively, at $y = 0$.

There are in addition the boundary conditions at $z = L_1$ or $y = 0$, and at $y = L_2$ or $x = l'$:

$$C_z(L_1) = C_y(0) \tag{11}$$

$$D_z\left(\frac{\partial C_z}{\partial z}\right)_{z=L_1} = D_y'\left(\frac{\partial C_y}{\partial y}\right)_{y=0} \tag{12}$$

$$C_y(L_2) = C_x(l') \tag{13}$$

$$-D_y'\left(\frac{\partial C_y}{\partial y}\right)_{y=L_2} = vC_x(l') \tag{14}$$

By combining these relations with eqns. 4 and 9, $C_x(l')$ is found:

$$\begin{aligned} C_x(l') = {} & (m/aD_y'q')\{\cosh qL_1 [\sinh q'L_2 + (v/D_y'q') \cosh q'L_2] + \\ & G \sinh qL_1 [\cosh q'L_2 + (v/D_y'q') \sinh q'L_2]\}^{-1} \end{aligned} \tag{15}$$

where

$$G = D_z q/D_y' q' \tag{16}$$

Inverse Laplace transformation of this equation to find $c_x(l', t_{\text{tot}})$ is very difficult. It could be achieved only by using certain approximations, the first of which was to replace $\sinh \omega$ and $\cosh \omega$ both by $\exp(\omega)/2$, where ω represents qL_1 or $q'L_2$. For not too long times and not too short diffusion columns, this is a good approximation, as for $\omega = 1.5$ the error introduced is about 5%, and for $\omega = 3$ it is only 0.25%. These ω values fall within the realm of experimental practice. A second approximation was based on the fact that for high enough flow-rates $1 + v/D_y'q' \approx v/D_y'q'$. Using these approximations eqn. 15 becomes

$$C_x(l') = \frac{4m}{\dot{V}} \cdot \frac{\exp[-p^{\frac{1}{2}}(L_1/D_z^{\frac{1}{2}} + L_2/D_y'^{\frac{1}{2}})]}{1 + (D_z/D_y')^{\frac{1}{2}}} \tag{17}$$

and the p inverse transform gives the required function:

$$c_x(l', t_{\text{tot}}) = \frac{N}{t_{\text{tot}}^{3/2}} \cdot \exp[-(L_1/D_z^{1/2} + L_2/D_y'^{1/2})^2/4t_{\text{tot}}] \tag{18}$$

where

$$N = 2m\left(\frac{L_1}{D_z^{1/2}} + \frac{L_2}{D_y'^{1/2}}\right)\Big/\pi^{\frac{1}{2}}\,\dot{V}\left[1 + \left(\frac{D_z}{D_y'}\right)^{\frac{1}{2}}\right] \tag{19}$$

The analytical function describing the extra reversal peaks is found from eqn. 1 by putting in place of $c_x(l', t_{tot} - \tau)$ and $c_x(l', t_{tot} + \tau)$ the right-hand side of eqn. 18 with t_{tot} changed to $t_{tot} - \tau$ and $t_{tot} + \tau$, respectively.

The relation giving the height, h, of the extra peaks above the continuous chromatographic signal (taken as the baseline) at $\tau = t'_M$ is found from eqn. 1 by considering its last term as baseline c_b. Thus,

$$h \equiv (c_x - c_b)_{\tau = t'_M} = \frac{N}{(t_{tot} - t'_M)^{3/2}} \times$$

$$\exp\left[-(L_1/D_z^{1/2} + L_2/D_y'^{1/2})^2/4(t_{tot} - t'_M)\right] \tag{20}$$

and the plot of $\ln[h(t_{tot} - t'_M)^{3/2}]$ against $1/(t_{tot} - t'_M)$, as before[1], should be linear with slope $-(L_1/D_z^{1/2} + L_2/D_y'^{1/2})^2/4$.

Substituting eqn. 8 for D'_y in the above expression and knowing L_1 and L_2, as well as D_z and D_y pertaining to empty columns, the partition ratio k is calculated. Both D_z and D_y were found from the results of previous experiments[1] by correcting them at the temperatures of columns L_1 and L_2. For this correction the relation $D_1/D_2 = (T_1/T_2)^{3/2}$ was used, as the simple kinetic theory implies. Finally, from the value of k the adsorption equilibrium constant K can be calculated from the equation $K = k\varepsilon/(1 - \varepsilon) = k/r$.

Flow effects perturbing the data, such as eddying around the confluence and pressure effects at flow reversal, must be negligible, as the same technique applied in diffusion coefficient measurements gave results of high precision and accuracy.

EXPERIMENTAL

Materials

The solid adsorbent was aluminium oxide, 60–72 mesh (Type F-1 from Applied Science Labs., State College, PA, U.S.A.). The carrier gas was helium of 99.99% purity (Aga Chropei, Athens, Greece). The various solutes were methane (99.99%), ethene (99.98%), propene (99.7%), but-1-ene (99.9%) (all from Matheson Gas Products, East Rutherford, NJ, U.S.A.), and ethane (puriss) and *n*-butane (pract) (from Fluka, Buchs, Switzerland).

Apparatus and procedure

The experimental set-up and the procedure were as already described[1], except for the following. The diffusion column was 70 cm long (4 mm I.D.), with its lower part, L_2 = 17 cm, filled with aluminium oxide and placed within the chromatographic oven, while the upper part, L_1 = 53 cm, was empty and outside the oven, at ambient temperature. The two lengths l and l' of the chromatographic column were 103 cm (4 mm I.D.). Temperature variations in the oven were less than ±0.1°C. The carrier gas flow-rate (corrected at column temperature) was in the range 0.37–0.50 cm^3 sec^{-1}.

Before the experiments, the adsorbent was heated at 674°K for 24 h with carrier gas flowing in the column $l + l'$.

The void fraction, ε, in the filled column part L_2 (Fig. 1) was determined by a standard method[2] and found to be 0.13.

RESULTS AND DISCUSSION

The values of the partition ratio k calculated by the method outlined in the theoretical section are given in Table I. The corresponding equilibrium constants K are not given, as they can be found from the k values after division by $r = 6.69$. These constants decrease with increasing temperature and increase with increasing number of carbon atoms in the molecule. They also increase in going from saturated to unsaturated hydrocarbons. All of these results are in accord with expected trends.

TABLE I

PARTITION RATIOS FOR ADSORPTION OF VARIOUS HYDROCARBONS ON ALUMINIUM OXIDE FROM HELIUM, AT VARIOUS TEMPERATURES

The void fraction of the bed was 0.13.

Substance	*T* (°*K*)	*k*	*Substance*	*T* (°*K*)	*k*
Methane	323.2	0.792	Ethene	323.7	15.0
	336.4	0.756		337.7	11.5
	346.4	0.615		352.0	8.28
	362.8	0.537		364.6	7.01
Ethane	325.8	6.22		375.6	5.23
	336.3	5.60	Propene	298.2	103
	347.9	4.86		324.0	46.9
	358.0	4.25		339.3	15.1
	371.9	3.78		352.3	12.7
n-Butane	358.5	17.1		359.8	9.80
	374.3	14.9	But-1-ene	325.8	157
	394.4	10.0		346.6	69.3
	409.8	7.30		360.4	43.1
				372.8	28.3
				392.9	11.9

The partition ratios for methane are small, but not zero as usually assumed by chromatographers, who use this gas to determine the gas hold-up time of a gas–solid chromatographic column with a flame-ionization detector (FID). With a column such as that used in the present work methane would give a value for the hold-up time that is greater than the actual value by 54–79%, depending on the temperature.

From the variation of the adsorption equilibrium constant with temperature, the differential enthalpies (heats) and entropies of adsorption can be determined as follows. Adsorption equilibrium is described by the equality

$$\mu_s^\ominus + RT \ln q_y = \mu_G^\ominus + RT \ln p_y$$

where the left-hand side is the chemical potential of the solute in the adsorbed state with a hypothetical standard state of $q_v = 1$ mol cm^{-3}, and the right-hand side is the chemical potential in the gas phase with $p_v = 1$ atm as its standard state. Denoting $\mu_s^\ominus - \mu_G^\ominus$ by $\Delta G^\ominus$ (standard Gibbs free energy change), substituting p_v from the ideal gas law $p_v = c_v RT$, and using the definition $K = q_v/c_v$, one obtains

$$K = RT \exp\left(-\frac{\Delta G^\ominus}{RT}\right) = RT \exp\left(\frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT}\right) \tag{21}$$

Rearranging and taking logarithms, the following linear form results:

$$\ln (K/T) = \ln R + \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{R} \cdot \frac{1}{T} \tag{22}$$

and thus a plot of ln (K/T) against $1/T$ will give $\Delta H^\ominus$ from the slope and $\Delta S^\ominus$ from the intercept, it being understood that the range of T is narrow enough for $\Delta H^\ominus$ and $\Delta S^\ominus$ to be regarded as independent of temperature. Table II lists the enthalpies and entropies of adsorption determined by this method, and Fig. 2 gives an example of plotting the experimental results according to eqn. 22. By choosing a different standard state for the adsorbed solute, such as the adsorbed state in equilibrium with gas at pressure p_y, only the values of $\Delta S^\ominus$, but not those of $\Delta H^\ominus$, will change. Therefore, the values of $\Delta S^\ominus$ given in Table II should be regarded as relative.

TABLE II

ENTHALPIES AND ENTROPIES OF ADSORPTION OF VARIOUS HYDROCARBONS ON ALUMINIUM OXIDE FROM HELIUM

Values ± standard errors.

Substance	$-\Delta H^\ominus$ *(kJ mol^{-1})*	$-\Delta S^\ominus$ *(J K^{-1} mol^{-1})*
Methane	13 ± 2	143 ± 6
Ethane	14.1 ± 0.4	129 ± 1
n-Butane	24 ± 3	144 ± 7
Ethene	23 ± 1	149 ± 3
Propene	38 ± 4	189 ± 12
But-1-ene	43 ± 2	190 ± 6

The main merits of the present method for determining adsorption equilibrium constants are reflected in the differential heats of adsorption found, which correspond to isosteric of zero coverage more closely than values determined from conventional gas chromatographic data by plotting ln V_N or ln (V_N/T) against $1/T$. This is so because the total amount of solute injected into the system was of the order of 10^{-5} mol and, owing to its diffusional distribution with distance along the column $L_1 + L_2$, only a small fraction of this was located over the adsorbent bed each time. Moreover, the distribution along the adsorbent was almost uniform all the time, contrasting with that of chromatographic elution, where the whole amount of solute

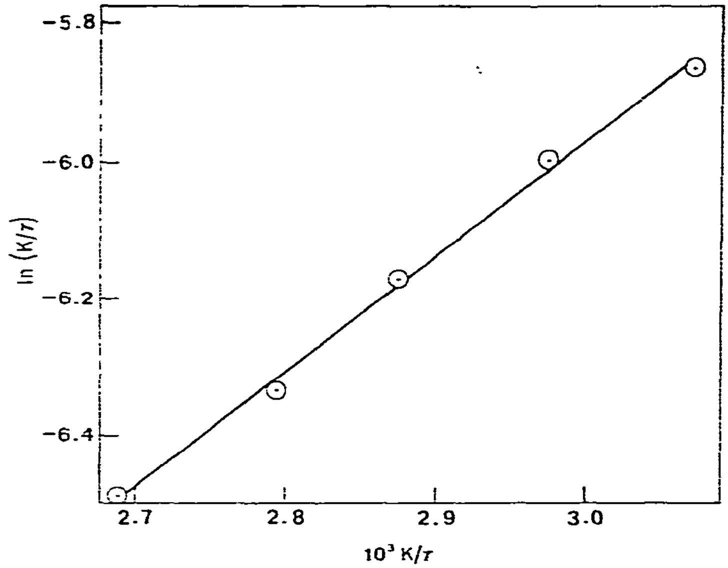

Fig. 2. Plot of the data for adsorption of ethane on aluminium oxide according to eqn. 22.

moves along the column as a relatively narrow band, with much higher local concentrations at a certain region of the adsorbent and zero concentration at others.

A comparison of the present results with others in the literature is not possible, not only because adsorption data for hydrocarbons with 1–4 carbon atoms are scarce, but also because on aluminium oxide these data vary widely with the origin of this adsorbent and with the temperature of its activation. The latter has amply been shown before[3].

A second notable aspect of the data in Table II is that the differential entropies of adsorption do not seem to bear any linear dependence on the corresponding $\Delta H^{\ominus}$ values (compensation effect), as is almost always the case with ΔS and ΔH values determined chromatographically. An explanation of the compensation effect[3] was that it is due to the chromatographic process itself combined with the heterogeneity of the surface. There is no chromatography within the diffusion column in the present case, and the very small fractional coverage of the surface does not permit heterogeneity to come into play. Thus, the results presented in Table II support in a way the previous explanation[3] of the compensation effect and, on the other hand, seem to be of more fundamental significance, as they are not influenced by the chromatography itself. They are, so to speak, heats and entropies of adsorption determined by gas chromatography instrumentation but "without chromatography".

SYMBOLS

a	cross-sectional area of column L_1 (cm).
c_b	concentration defined by the last term of eqn. 1 (mol cm^{-3}).
c_x, c_y, c_z	concentrations of the solute vapour in the regions x, y and z of the cell (Fig. 1), respectively (mol cm^{-3}).

C_x, C_y, C_z	Laplace transforms of c_x, c_y, c_z, respectively, with respect to t_{tot}.
D_y, D_z	diffusion coefficient of the solute in the carrier gas, within the region y and z of the diffusion column, respectively (cm^2 sec^{-1}).
D'_y	effective diffusion coefficient defined by eqn. 8 (cm^2 sec^{-1}).
G	function defined by eqn. 16 (dimensionless).
h	height above the baseline defined by eqn. 20 (mol cm^{-3}).
k	partition ratio of solute (dimensionless).
K	adsorption equilibrium constant (partition coefficient) of solute (dimensionless).
l, l'	lengths of the two sections of the chromatographic column (Fig. 1) (cm).
L_1, L_2	lengths of the two sections of the diffusion column (Fig. 1) (cm).
m	mass of solute injected (mol).
N	constant defined by eqn. 19.
p	transform parameter.
p_y	partial pressure of the solute in the y region of the gas phase (atm).
q, q'	parameters defined by eqns. 5 and 10, respectively (cm^{-1}).
q_y	concentration of solute in the adsorbed state per unit volume of solid (mol cm^{-3}).
r	volume ratio of solid and gas phases.
t	time measured from the last reversal of the gas flow (sec).
t_{tot}	total time passed from the injection of solute to the last reversal of the gas flow (sec).
t_M, t'_M	gas hold-up time of column section l or l', respectively (sec).
v	linear velocity of the carrier gas in the chromatographic column (cm sec^{-1}).
$\dot{V}$	volume flow-rate of carrier gas (cm^3 sec^{-1}).
V_N	net retention volume (cm^3).
x, y, z	distance co-ordinates defined in Fig. 1 (cm).
ε	void fraction of column section L_2 (dimensionless).
$\mu_G^\ominus$, $\mu_s^\ominus$	chemical potential of the solute in its standard states of the gas and of the adsorbed state, respectively (J mol^{-1}).
τ	time measured from the last reversal of the flow diminished by the gas hold-up time in the flow direction, eqn. 2 (sec).

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