Determination of adsorption equilibrium constants by reversed-flow gas chromatography

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Abstract

Reversed-flow gas chromatography was employed to determine adsorption equilibrium constants.

Keywords: Adsorption equilibrium constants; Ethane; Ethene; Propene; Ethyne

1. Introduction

Reversed-flow gas chromatography [1] offers advantages for physico-chemical measurements. In recent years, it has been more and more studied in many countries, but in China it is still a new field. It has become more and more important owing to the very precise and accurate results obtained, relatively cheap instrumentation and very simple experimental set-up. It may be employed as a means of studying surface-catalysed chemical reactions and measuring adsorption equilibrium constants. Using reversed-flow GC, the adsorption equilibrium constants of a few organic gases on the absorbent Al_2O_3 were determined. A new method of determining the adsorption equilibrium constant was established on the basis of studies of physical adsorption

phenomena by GC. The different conditions that influence the adsorption equilibrium constant were examined to verify the relevant theory of physical adsorption.

2. Experimental

2.1. Apparatus

The apparatus (SP-2305; Analysis Instrument Factory, Beijing, China) is slightly modified from a common GC system with a high-sensitivity detection device, such as a flame ionization detector, as shown in Fig. 1. Fig. 2 shows the sampling cell for studying mass transfer phenomena across a phase boundary near the junction of the diffusion and the sample columns. In this work, the effective lengths (which can be determined by a simple experiment [2]) of L_1 and L_2 are 15.6 and 54.5 cm, respectively.
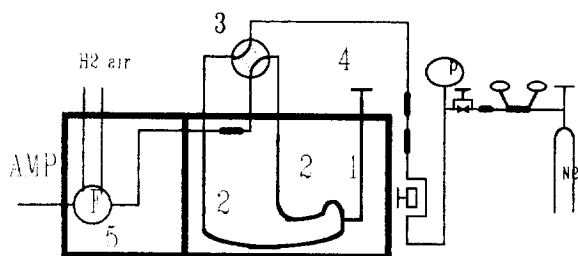
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Fig. 1. Schematic diagram of SP-2305 system for use with the reversed-flow technique. 1 = Diffusion column; 2 = sampling column; 3 = four-port valve; 4 = solute injector; 5 = detector.

2.2. Theoretical analysis

In the region y (see Fig. 2) of the diffusion column (empty), the diffusion equation is

$$\frac{\partial C_y}{\partial t_0} = D\left(\frac{\partial^2 C_y}{\partial y^2}\right) \tag{1}$$

where D is the diffusion coefficient of the sample gas in the carrier gas and C_y is the concentration of the sample gas in the section y. When the solute was introduced as a pulse at the injection point, $y = L_2$ and the boundary condition under the initial condition is

$$C_y(y,0) = \left(\frac{m}{a_G}\right)\delta(y - L_2) \tag{2}$$

where m is the amount of solute injected and a_G is the volume of gas phase per unit length of column. The solution at $y = 0$ is

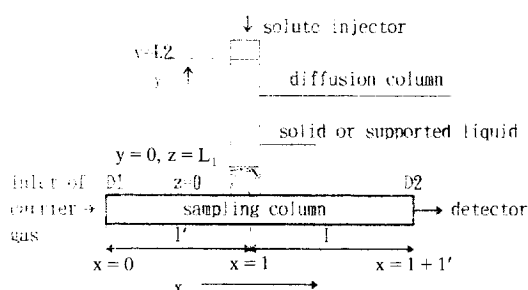$$\overline{C_y'}(0) = \frac{m}{a_G D \cosh qL_2} - \bar{C}_y(0)q \tan hqL_2 \tag{3}$$

Fig. 2. Sampling cell for studying mass transfer phenomena across the phase boundary near the junction of the diffusion and the sampling columns.

where $\bar{C}_y(0)$ is the t_0 Laplace-transformed function C_y at $y = 0$, $\bar{C}_y'(0)$ the derivative $(d\bar{C}_y/dy)_{y=0}$ and q is given by

$$q^2 = \frac{p_0}{D} \tag{4}$$

where p_0 is the transform parameter with respect to t_0.

In the region z of the diffusion column (filled), the mass balance equation is

$$\frac{\partial C_z}{\partial t_0} = D\left(\frac{\partial^2 C_z}{\partial Z^2}\right) - K_S \cdot \frac{A_S}{V_G'}(C_S^* - C_S) \tag{5}$$

where C_z is the gaseous concentration of the solute in section z, V_G' the gaseous volume of the length L_1, K_S the overall mass transfer coefficient between the gas and the solids, A_S the total surface area and c_S^* and C_s equilibrium, and non-equilibrium adsorbed concentration, respectively.

The rate of change of C_S is given by

$$\frac{\partial C_S}{\partial t_0} = K_S \cdot \frac{A_S}{V_S}\left(C_S^* - C_S\right) \tag{6}$$

where V_S is the total volume of the solid. The system of partial differential Eqs. 5 and 6 is solved by applying first Laplace transformations with respect to t_0 under the initial condition

$$C_z(z,0) - C_S(z,0) = 0 \tag{7}$$

and eliminating C_S between the transformed equations:

$$\frac{d^2\bar{C}_z}{dz^2} - q_z^2\bar{C}_z = 0 \tag{8}$$

where $\bar{C}_z$ is the t_0-transformed function C_z (z,t_0) and is given by

$$q_z^2 = \frac{1}{D}\left[p_0 + \frac{\left(\dfrac{K_S K A_S}{V_G'}\right)p_0}{p_0 + \dfrac{K_S A_S}{V_S}}\right] \tag{9}$$

K being the partition coefficient in the linear isotherm:

$$K = \frac{C_S^*}{C_z} \tag{10}$$

The solution of Eq. 8 using further transformation with respect to z is

$$\bar{C}_z = \bar{C}_z(0) \cosh q_z z + \frac{\bar{C}_z'(0)}{q_z} \cdot \sinh q_z z \qquad (11)$$

where $\bar{C}_z(0)$ and $\bar{C}_z'(0)$ are the t_0-transformed functions $C_z(0)$ and $(dC_z/dz)_{z=0}$, respectively. Eq. 11 is subject to two sets of boundary conditions. The first set is at $z = 0$:

$$\bar{C}_z(0) = \bar{C}(l', p_0)$$

$$a_G' D \left(\frac{\partial \bar{C}_z}{\partial z} \right)_{z=0} = a_G V \bar{C}(l', p_0) \qquad (12)$$

a_G' and a_G being the void cross-sectional areas in the filled section L_1 and in the sampling column, respectively. Using this, Eq. 11 becomes

$$\bar{C}_Z = \bar{C}\left(p', p_0 \right) \times \cosh q_z z + \frac{a_G V}{a_G' D q_z} \cdot \sinh q_z z \right) \qquad (13)$$

Then, using the second set of boundary conditions which links together Eq. 13 of region z and Eq. 3 of region y, $\bar{C}_z(L_1) - \bar{C}_y(0)$

$$a_G' \left(\frac{\partial \bar{C}_z}{\partial z} \right)_{z=L_1} = a_G \left(\frac{\partial \bar{C}_y}{\partial y} \right)_{y=0} \qquad (14)$$

and they lead to the equation

$$\bar{C}(l', p_0) = \frac{m}{D q_z \cosh q L_2}$$

$$\times \left[a_G' \sinh q_z L_1 + \frac{a_G v}{D q_z} \cdot \cosh q_z L_1 + \frac{a_G q}{a_G' q_z} \right.$$

$$\left. \cdot \tanh q L_2 \left(a_G' \cosh q_z L_1 + \frac{a_G v}{D q_z} \cdot \sinh q_z L_1 \right) \right]^{-1} \qquad (15)$$

The usual approximation $(v/D q_z) \gg 1$ permits the omission of the terms $a_G' \sinh q_z L_1$ and $a_G' \cosh q_z L_1$, thus simplifying Eq. 15 to

$$C(l', p_0) = \frac{m}{V} (\cosh q_z L_1 \cdot \cosh q L_2$$

$$+ \frac{a_G q}{a_G' q_z} \cdot \sinh q_z L_1 \cdot \sinh q L_2)^{-1} \qquad (16)$$

where $\dot{V}$ is the volume flow-rate of carrier gas. Then, applying the approximation [3] of replac-

ing both $\sinh(x)$ and $\cosh(x)$ in Eq. 16 by $\exp(x)/2$, we obtain

$$C(l', t_0) = \frac{N_7}{t_0^{3/2}} \cdot \exp\left(-\frac{L_{eff}^2}{4 D t_0} \right) \qquad (17)$$

where N_7 is a constant and L_{eff} the effective length of the column, given by

$$L_{eff} = L_2 + L_1 (1 + k)^{1/2} \qquad (18)$$

Then using the relation $h = 2(C(l', t_0)$ [4] and taking logarithms, Eq. 17 becomes

$$\ln(h t_0^{3/2}) = \frac{L_{eff}^2}{4 D t_0} - \ln\left(\frac{1}{2 N_7} \right) \qquad (19)$$

where h is the height of the peaks with respect to t_0. Plotting $\ln(h t_0^{3/2})$ vs. $1/t$, from the slope and the known lengths L_1 and L_2, k can be determined. Finally, using the relation

$$K = \frac{k \varepsilon}{(1 - \varepsilon)} \qquad (20)$$

ε (which can be obtained by a standard method [5]) being the void fraction in the filled column section L_1, the adsorption equilibrium constant, K, can be calculated.

2.3. Procedure

Under certain chromatographic conditions [N_2 (purity 99.99%) as the carrier gas at a flow-rate of 30–35 ml/min], a small amount of a simple hydrocarbon gas (about 0.8–2.0 ml) was injected into the diffusion column of effective length 98.7 cm × 4 mm I.D. After a certain time during which no signal was noted, an asymmetric concentration–time curve for the sample gas was recorded, usually decaying slowly. At a certain known time (from the moment of injection), the direction of the carrier gas was reversed by switching valves from the position of the dashed line and the time interval was t' ($t' < t_{r'}$ and $t' < t_r$, $t_{r'}$ and t_r were the ideal retention times on the sampling column sections l and l', respective-
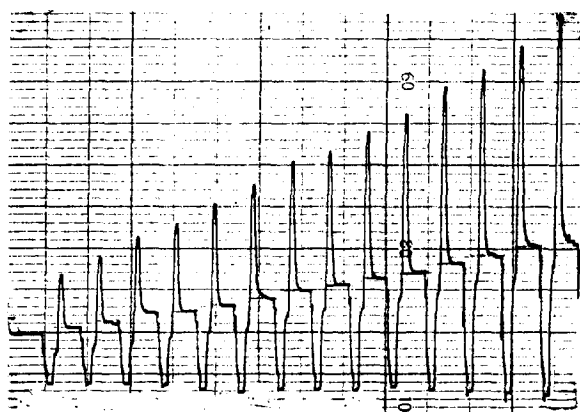
Fig. 3. Reversed-flow chromatographic plot.

ly). The reversal was repeated several times and a series of sample peaks were thus obtained.

3. Results and discussion

3.1. Determination of adsorption equilibrium constant of ethane

Following the above experimental procedure, a series of reversed-flow chromatographic peaks of ethane were obtained (Fig. 3). After measuring the height h of each sample peak, then using the relation $h = 2c(l',t_0)$ and with the value of $1/t_0$ and $\ln(ht_0^{3/2})$ calculated, the $\ln(ht_0^{3/2})$ versus $1/t_0$ graph can be plotted easily. Table 1 gives the values of h, t_0, $1/t_0$ and $\ln(ht_0^{3/2})$.

From the $\ln(ht_0^{3/2})$ versus $1/t_0$ plot, the slope is obtained: $K_a = -1.30 \cdot 10^4$, and then from the relationship

$$K_a = \frac{-L_{eff}^2}{4D}$$

L_{eff} can be calculated:

$$L_{eff} = \sqrt{-4DK_a} = [-4 \cdot 0.135 \cdot (-1.30 \cdot 10^4)]^{1/2}$$
$$= 83.8 \text{ cm}$$

Then, using Eq. 18, the partition ratio k can also be obtained:

$$k = \left(\frac{L_{eff} - L_2}{L_1}\right)^2 - 1 = \left(\frac{83.8 - 54.5}{15.6}\right)^2 - 1 = 2.52$$

Finally, from the value of k, the absorption equilibrium constant K can be found using Eq. 20. In this work, the absorbent was Al_2O_3 of 55–75 mesh. Because the same absorbent with the same mesh is used, the value of K is directly proportional to k, so the variation of k is the same as that of K.

3.2. Influence of the amount of sampling gases on the value of k (K)

In theory, the value of K has nothing to do with the amount of sample gases. However, when the sample is absorbed, it diffuses in the carrier gas. The process of diffusion is influenced by the amount of sample. Hence it is necessary to avoid the influence of the amount of sample. Keeping the other conditions unchanged except the amount of sample and repeating the experiment until the value of k is unchanged within the experimental error, a suitable amount or a suitable range of amount of ethene sample may be found. Table 2 gives the experimental data with

Table 1
Values of h, t_0, $1/t_0$ and $\ln(ht_0^{3/2})$ for various peaks

Parameter	Peak No.							
	1	3	5	7	9	11	13	15
t_0 (min)	43	46	49	52	55	58	61	64
h (cm)	2.79	3.47	4.29	5.13	5.84	6.25	7.67	8.72
$1/t_0$ (10^{-1}s^{-1})	3.8	3.62	3.40	3.21	3.03	2.87	2.73	2.60
$\ln(ht_0^{3/2})$	12.81	13.13	13.44	13.70	13.92	14.14	14.35	14.55

Table 2
Values of k for ethene on Al_2O_3

Volume of sample (ml)	T (vaporizer) (°C)	T (column) (°C)	D (sample) (cm² s⁻¹)	k
1.60	25.4	100.0	0.135	2.52
1.40	26.0	99.8	0.135	2.60
1.20	26.7	99.3	0.136	2.60
1.00	26.8	99.5	0.136	2.65
0.80	25.0	100.3	0.135	2.66

ethene as the sample. By analysing the data, amounts in the range 0.8–1.6 ml are suitable for the experimental requirements. In the same way, the amount of sample of ethyne and propene can also be found. In our experiment, the optimum amounts of the three sample compounds are 1.2, 1.4 and 1.4 ml, respectively.

3.3. Influence of temperature on the value of k

Keeping the other conditions unchanged except the temperature, the values of k of the above samples were determined (Table 3). There is an obvious law deriving from the data: the value of k decreases when the temperature increases, which is consistent with the occurrence of adsorption. Physical adsorption is an exothermic process because the entropy of adsorption decreases when the molecules of the sample are adsorbed on the absorbent in a regular manner. That is, raising the temperature is harmful to the adsorption, so the adsorption equilibrium constant is certain to decrease.

3.4. Influence of carbon number of the sample on the value of k

The value of k of hydrocarbon gases with the same degree of saturation is related to the number of carbons in the molecule, keeping the other conditions unchanged. The law is that the value of k decreases when the number of carbons in the sample molecule rises. This can be seen from the data in Table 4. When the number of carbons increases, the neighbouring carbon ac-

Table 4
Values of k for samples with different numbers of carbon atoms

Sample	T (column) (°C)	T (vaporizer) (°C)	k
Ethene	121.5	27.8	1.91
Propene	119.0	24.0	2.34
Ethene	99.3	26.7	2.60
Propene	102.3	23.8	4.15
Ethene	90.0	27.7	4.02
Propene	89.5	25.0	6.11

Table 3
Values of k for ethene, propene and ethyne on Al_2O_3 at different temperatures

Ethene			Propene			Ethyne		
T (column) (°C)	T (vaporizer) (°C)	k	T (column) (°C)	T (vaporizer) (°C)	k	T (column) (°C)	T (vaporizer) (°C)	k
121.5	27.8	1.91	119.0	24.0	2.34	119.0	24.0	2.34
109.7	26.0	2.72	102.3	23.8	4.15	108.0	23.9	41.98
99.3	26.7	2.60	89.5	25.0	6.11	101.0	25.6	46.85
90.0	27.7	4.02	70.4	25.2	9.11	89.0	25.0	53.96

quires more negative charge because of the super-conjugation of radical "-CH$_2$". The Van der Waals force between the sample and the absorption increase, so the value of k also increases. Table 4 gives a comparison between the values of k for ethene and propene under the experimental conditions.

3.5. Influence of degree of saturation on the value of k

Table 5 gives the values of k for ethene and ethyne under the same experimental conditions.

Table 5
Values of k for ethene and ethyne under same experimental conditions

Sample	T (column) (°C)	T (vaporizer) (°C)	k
Ethene	121.5	27.8	1.91
Ethyne	121.0	23.6	30.75
Ethene	109.7	26.0	2.22
Ethyne	108.0	23.9	41.98
Ethene	99.3	26.7	2.60
Ethyne	101.0	25.6	46.85

It is obvious that the value of k for ethyne is much larger than that for ethene. The reason is also obvious: the electrical density between the two carbons of ethyne is much larger than that of ethene because of their different degrees of saturation. This causes the Van der Waals force between the molecules of ethyne and adsorption to be much larger than that between the molecules of ethyne and adsorption and the molecules of ethyne are desorbed from the adsorbent with greater difficulty.

References

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