Journal of Chromatography, 151 (1978) 291–297

CHROM. 10,491

DESORPTION KINETIC PARAMETERS AND ADSORPTION THERMODYNAMIC PARAMETERS DETERMINED SIMULTANEOUSLY BY STOPPED-FLOW GAS CHROMATOGRAPHY

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(First received June 6th, 1977; revised manuscript received August 9th, 1977)

SUMMARY

The use of the equations derived in a previous paper has led to the determination of rate constants for desorption, and of equilibrium constants for adsorption, of heptane on two kinds of active sites of modified alumina and of porous glass. Experiments at various temperatures have permitted the calculation of desorption activation energies and entropies of activation from the variation of rate constants with temperature, as well as the calculation of adsorption enthalpies and entropies from the variation of equilibrium constants with temperature.

INTRODUCTION

In a previous paper[1] we reported the derivation of the equation

$$f = Y_1 \exp(-k_{-1}t) + Y_2 \exp(-k_{-2}t) \tag{1}$$

which applies to non-equilibrium stopped-flow gas chromatography, taking place on two kinds of adsorption sites. The functions Y_1 and Y_2 are such that:

$$Y_1 + Y_2 = \frac{mrt_s\,(k_{-1}K_1 + k_{-2}K_2)}{1 + r\,(K_1 + K_2)} \cdot \exp\left[-\,(k_{-1}K_1 + k_{-2}K_2)\,\frac{V_s}{\dot{V}}\right] \tag{2}$$

and

$$\frac{Y_1}{Y_2} = \frac{k_{-1}K_1}{k_{-2}K_2} \cdot \frac{1 - \dfrac{k_{-2}K_2V_s}{\dot{V}} \cdot \dfrac{k_{-1} + k_{-2}}{k_{-1} - k_{-2}}}{1 + \dfrac{k_{-1}K_1V_s}{\dot{V}} \cdot \dfrac{k_{-1} + k_{-2}}{k_{-1} - k_{-2}}} \tag{3}$$

The various symbols are defined as follows: f = area (mole) under the curve of a stop-peak; k_{-1}, k_{-2} = rate constants (sec^{-1}) for desorption from sites 1 and 2; K_1, K_2 = dimensionless equilibrium constants for adsorption (partition coefficients) on sites 1 and 2; m = total amount (mole) of injected vapour; r = volume ratio of solid and gas phases; t = time interval (sec) from the beginning of the carrier gas flow to the beginning of the stopped-flow interval; t_s = stopped-flow time (sec); $\dot{V}$ = volume flow-rate (cm^3/sec) of carrier gas; V_s = total volume (cm^3) of solid adsorbent.

In the present paper we use the above equations to determine k_{-1}, k_{-2}, K_1 and K_2 from experimental data for the adsorption–desorption of heptane on alumina modified with potassium chloride and on porous glass. From the variation with temperature of these rate and equilibrium constants, activation energies and entropies of desorption, as well as enthalpies and entropies of adsorption, are computed.

EXPERIMENTAL

Materials

Aluminium oxide, Type F-1, pH ≈ 9.5, 100–120 mesh (Matheson, Coleman & Bell, East Rutherford, N.J., U.S.A.), and porous glass, pH ≈ 2.3, 80–100 mesh (Applied Science Labs., State College, Pa., U.S.A.), were used as solid adsorbents. "Suprapur" potassium chloride and "Uvasol" heptane (E. Merck, Darmstadt, G.F.R.) were used as the modifier and adsorbate, respectively. Methane (99.99% purity; Matheson) was used for the determination of the dead volume of the chromatographic columns.

In all of the experiments nitrogen (99.98% purity) was used as the carrier gas. This was obtained from AGA Chropei (Athens, Greece) and dried by passing it through a tube containing 4A molecular sieve.

Apparatus

A Pye-Unicam Series 104 gas chromatograph with a flame ionization detector was used in all of the experiments. This was connected to a Hewlett-Packard Model 3370B electronic integrator for the determination of the area under the curve of each stop-peak, and to a Goerz RE 532 recorder equipped with a disc integrator. The latter was used for continuous recording of the chromatographic signal and for the determination of the total area under the curve of the eluted adsorbate, although this last determination is not absolutely necessary.

A Pye-Unicam Model 12684 gas-flow controller was used for maintaining a constant flow-rate through the chromatographic column, independently of variations in temperature. Two shut-off valves, one on each side of the gas-flow controller and operated simultaneously, served to stop and restore the carrier gas flow through the column.

The oven temperature was read on a calibrated mercury thermometer. Temperature variations in each experiment were less than ±0.1 °C. Volume flow-rates were measured at the end of the column by means of a bubble-flowmeter; they were corrected for pressure drop along the column (of the order of 10^3 N/m^2) measured by an open mercury manometer, and they were finally corrected to column temperature.

Two columns were used, a stainless-steel column (1.2 × 0.4 cm I.D.) filled with Al_2O_3–10% (w/w) KCl (0.41 g), and a glass column (2.7 × 0.4 cm I.D.) filled with porous glass (0.29 g).

Preparation of the modified alumina

Aluminium oxide (9 g) was sieved (100–120 BSS mesh) and then impregnated with a solution of potassium chloride (1 g) in distilled water (20 cm^3). After 15 h the resulting mixture was evaporated to a heavy slurry on a steam-bath. The slurry was spread on a filter paper and allowed to dry for a while before being heated in an oven at 373 °K for 30 min. It was then sieved (100–120 BSS mesh) and stored. This stationary phase is referred to as Al_2O_3–10 % (w/w) KCl or as modified alumina.

Conditioning of the columns and procedure

Desorption experiments were performed using both columns (run in nitrogen) after activation at 673 °K for 2 h and conditioning *in situ* at 373 °K for 24 h, in a nitrogen stream. The range of the carrier gas flow-rates used in the experiments was 0.267–0.750 cm^3/sec, the temperature range being 373–403 °K. Each temperature change was followed by a conditioning period of at least 12 h.

A small amount (*ca.* 1 mm^3) of heptane was injected on to the column and the carrier gas flow was immediately stopped, thus allowing the adsorbate to equilibrate between the gas and the solid phases at the inlet of the chromatographic column. It was found that a period of 135 min was necessary for this equilibration, after which the gas flow through the column was restored. A chromatographic signal was immediately recorded, having a sharp front profile and a long tailing. While the signal was decaying, the flow of the carrier gas was stopped and then restored after a 2 min interval, and this was repeated noting the time of each stop. Following each restoration of the carrier gas flow, a sharp symmetrical peak (stop-peak) was detected, which had a well defined retention time; its area (mV · sec) was determined and printed by the electronic integrator.

RESULTS AND DISCUSSION

The area of each stop-peak recorded by the instrument is λf, where f is given by eqn. 1 and λ is a proportionality constant. The actual value of this constant is not required for the calculation of k_{-1}, k_{-2}, K_1 and K_2 by means of eqns. 1, 2 and 3, as has been described[1]. Alternatively, one can normalize each stop-peak area, dividing it by the total area under the elution curve of the adsorbate, as recorded by the second integrator. The result is a relative (dimensionless) area, $f_{rel.}$, which is equal to f/f_{total}.

According to eqn. 1, a plot of $\ln f_{rel.}$ against t will yield a curve, and, if k_{-1} and k_{-2} are sufficiently different, the plot will become linear after a certain time, because the term with the greatest value of k (conventionally taken as k_{-1}) becomes negligibly small. An example is given in Fig. 1. The slope of the last linear section gives $-k_{-2}$ and its intercept with the y axis equals $\ln (Y_2/f_{total})$. A second straight line is constructed by plotting against t the logarithm of the points calculated from the difference between the experimental points and those found by extrapolation of the first straight line. The slope of the second line gives $-k_{-1}$ and its y intercept equals $\ln (Y_1/f_{total})$. The two rate constants of desorption, k_{-1} and k_{-2}, are thus determined.

The two equilibrium constants, K_1 and K_2, at a particular temperature, can be determined from kinetic runs at different flow-rates $\dot{V}$, by plotting $\ln [(Y_1 + Y_2)/f_{total}]$ against $1/\dot{V}$. According to eqn. 2, this plot should again be linear with slope $-(k_{-1}K_1 + k_{-2}K_2)V_s$, where V_s is known and k_{-1} and k_{-2} have already been determined. We thus have an algebraic equation in K_1 and K_2. A second equation is provided by eqn. 3, where the ratio Y_1/Y_2 is equal to $(Y_1/f_{total})/(Y_2/f_{total})$ determined from ex-

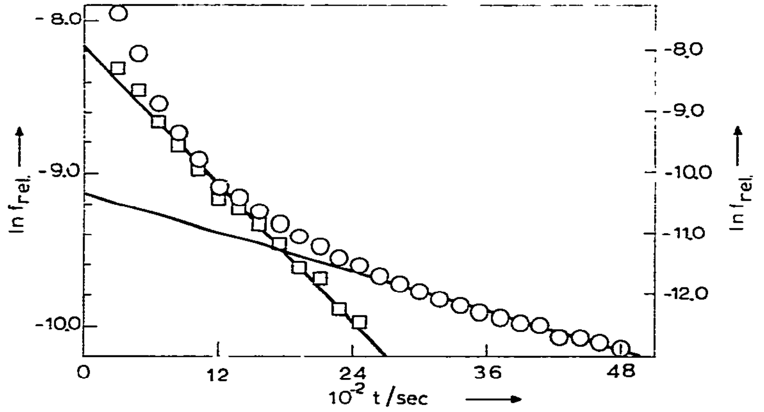

Fig. 1. Experimental data for desorption of heptane from modified alumina at 396.3 °K and with a carrier gas flow-rate of 0.315 cm^3/sec, plotted according to eqn. 1. ○, Experimental points (left ordinate); □, points calculated from the difference between the experimental points and those found by extrapolation of the last linear section (right ordinate).

TABLE I

RATE CONSTANTS FOR DESORPTION OF HEPTANE FROM Al_2O_3–10% (w/w) KCl AT VARIOUS TEMPERATURES

All errors given in this and the following tables are "standard errors".

T (°K)	10 $\dot{V}$ (cm^3/sec)	$10^3\,k_{-1}$ (sec^{-1})	$10^4\,k_{-2}$ (sec^{-1})
373.3	2.98	1.47 ± 0.03	1.57 ± 0.07
	4.12	1.43 ± 0.05	1.58 ± 0.05
	5.10	1.57 ± 0.05	1.55 ± 0.08
	6.18	1.63 ± 0.02	1.28 ± 0.03
	7.22	1.70 ± 0.03	1.38 ± 0.05
		Mean 1.56 ± 0.02	1.47 ± 0.03
379.1	3.18	1.35 ± 0.05	1.4 ± 0.1
	4.22	1.78 ± 0.05	1.72 ± 0.03
	5.23	1.75 ± 0.07	1.42 ± 0.07
	6.38	1.52 ± 0.03	1.65 ± 0.02
	7.45	1.85 ± 0.03	1.93 ± 0.03
		Mean 1.65 ± 0.02	1.62 ± 0.03
384.2	3.05	1.72 ± 0.07	1.57 ± 0.07
	4.27	1.67 ± 0.03	1.57 ± 0.07
	5.20	1.97 ± 0.05	1.95 ± 0.07
	7.37	1.63 ± 0.05	1.97 ± 0.07
		Mean 1.75 ± 0.03	1.77 ± 0.04
396.3	3.15	1.88 ± 0.05	2.13 ± 0.05
	4.45	2.02 ± 0.03	2.03 ± 0.05
	5.47	1.92 ± 0.03	2.02 ± 0.07
	6.45	2.10 ± 0.03	2.18 ± 0.05
	7.57	2.3 ± 0.1	2.13 ± 0.07
		Mean 2.05 ± 0.02	2.10 ± 0.03

perimental values. These two equations are then solved to give the values of K_1 and K_2.

The whole set of runs is then repeated at other temperatures.

In Tables I and II we have collected values of the rate constants for desorption at various temperatures and flow-rates. The existence of two rate constants shows the presence of two kinds of active sites, as reported in the literature for alumina[2,3] and for porous glass[4]. Small changes in the values of the rate constants of desorption with carrier gas flow-rate are probably due to small changes in the activation of the surface at each flow-rate, and also to random errors.

Table III gives the activation parameters for the desorption process from both active sites of the two adsorbents. They were determined from conventional Arrhenius plots of ln k_{-1} and ln k_{-2} against $1/T$. The mean values of k_{-1} and k_{-2} (*cf.* Tables I

TABLE II

RATE CONSTANTS FOR DESORPTION OF HEPTANE FROM POROUS GLASS AT VARIOUS TEMPERATURES

T (K)	*10 $\dot{V}$ (cm³/sec)*	*10^3 k_{-1} (sec⁻¹)*	*10^5 k_{-2} (sec⁻¹)*
376.2	3.47	1.93 ± 0.05	8.00 ± 0.02
	4.92	2.00 ± 0.05	6.83 ± 0.07
	6.13	2.13 ± 0.03	7.67 ± 0.03
		Mean 2.02 ± 0.03	7.50 ± 0.03
384.3	2.83	2.05 ± 0.08	8.00 ± 0.02
	4.25	2.3 ± 0.1	8.33 ± 0.03
	5.55	2.2 ± 0.1	8.17 ± 0.03
	6.78	2.13 ± 0.07	7.83 ± 0.02
		Mean 2.17 ± 0.04	8.08 ± 0.01
390.9	4.17	2.3 ± 0.1	8.8 ± 0.1
	5.42	2.4 ± 0.1	8.67 ± 0.03
	6.82	2.4 ± 0.1	8.33 ± 0.03
		Mean 2.37 ± 0.06	8.60 ± 0.04
398.7	2.73	2.45 ± 0.07	8.33 ± 0.05
	4.17	2.57 ± 0.07	9.17 ± 0.07
	5.72	2.67 ± 0.07	9.00 ± 0.05
	7.23	2.65 ± 0.07	9.67 ± 0.05
		Mean 2.59 ± 0.04	9.04 ± 0.03

TABLE III

ACTIVATION ENERGIES AND ACTIVATION ENTROPIES FOR DESORPTION OF HEPTANE FROM BOTH KINDS OF ACTIVE SITES 1 AND 2 OF Al_2O_3–10% (w/w) KCl AND OF POROUS GLASS

Surface	*E (kJ/mole)*		*ΔS^* (J/°K · mole)*	
	Sites 1	*Sites 2*	*Sites 1*	*Sites 2*
Al_2O_3–10% KCl	15.1 ± 0.8	18.8 ± 0.4	−269 ± 3	−277 ± 1
Porous glass	13.8 ± 0.8	10.5 ± 0.4	−270 ± 3	−307 ± 1

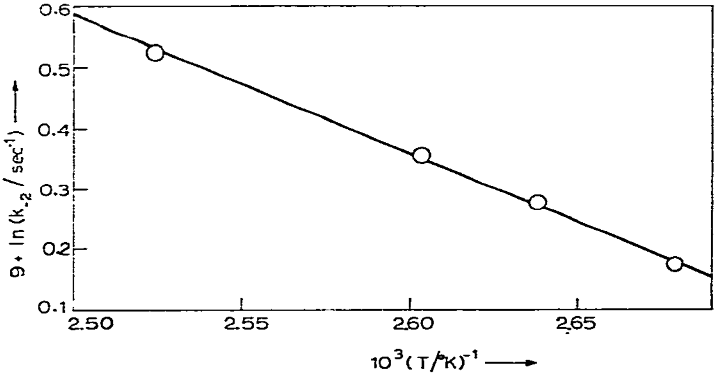

Fig. 2. An Arrhenius plot of the data for desoption of heptane from Al_2O_3–10% (w/w) KCl.

and II) were used, and an example is shown in Fig. 2. The values of activation energy found for the desoprtion of heptane from both adsorbent sites are small enough to place the process within the domain of physical adsorption.

Tables IV and V give the calculated equilibrium constants for adsorption (partition coefficients) on sites 1 and 2 of the adsorbents, at various temperatures. The

TABLE IV

EQUILIBRIUM CONSTANTS FOR ADSORPTION OF HEPTANE ON Al_2O_3–10% (w/w) KCl AT VARIOUS TEMPERATURES

T (°K)	K_1	K_2
373.3	1824	2793
379.1	1762	1996
384.2	1716	1662
396.3	1592	1471

TABLE V

EQUILIBRIUM CONSTANTS FOR ADSORPTION OF HEPTANE ON POROUS GLASS AT VARIOUS TEMPERATURES

T (°K)	K_1	K_2
376.2	545	1516
384.3	450	1428
390.9	354	1088
398.7	293	924

TABLE VI

ENTHALPIES AND ENTROPIES OF ADSORPTION OF HEPTANE ON BOTH KINDS OF ACTIVE SITES 1 AND 2 OF Al_2O_3–10% (w/w) KCl AND OF POROUS GLASS

Surface	*ΔH (kJ/mole)*		*ΔS (J/°K · mole)*	
	Sites 1	*Sites 2*	*Sites 1*	*Sites 2*
Al_2O_3–10% KCl	− 7.2 ± 0.3	−21 ± 4	43.1 ± 0.8	8 ± 2
Porous glass	−35 ± 2	−29 ± 4	−42 ± 4	−17 ± 3

values of K_1 and K_2 are large enough that, at equilibrium, most of heptane is in the adsorbed state.

Table VI compiles enthalpies and entropies of adsorption on the two kinds of sites of both adsorbents, determined from conventional Van't Hoff plots of ln K_1 and ln K_2 against $1/T$ (*cf.* Fig. 3). The enthalpies of adsorption are small enough to imply a physical adsorption process. The entropies of adsorption on Al_2O_3–10% (w/w) KCl are positive and this is hard to explain, since, as calculated here, they represent the change in entropy which would occur if 1 mole of adsorbate vapour was transferred from its standard state of 101.325 kN/m^2 (= 1 atm) at the temperature of the experiment to the adsorbed state corresponding to the working partial pressure. However, positive entropies of adsorption have also been observed[5].

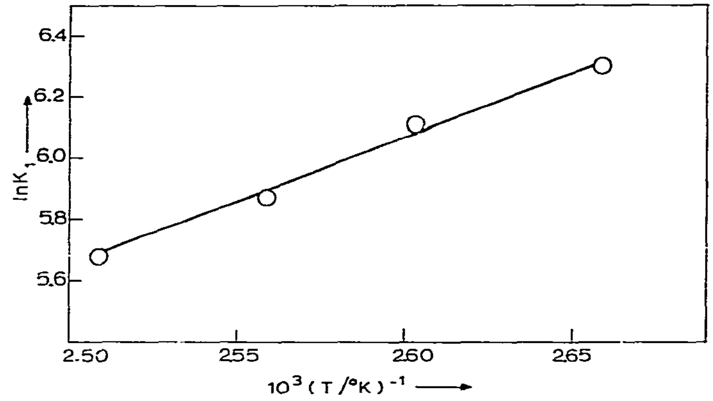

Fig. 3. A Van't Hoff plot of the data for adsorption of heptane on porous glass.

REFERENCES

1 N. A. Katsanos, G. Karaiskakis and I. Z. Karabasis, *J. Chromatogr.*, 130 (1977) 3.
2 R. J. Cvetanovic and Y. Amenomiya, *Advan. Catalysis*, 17 (1967) 103.
3 Y. Amenomiya and R. J. Cvetanovic, *J. Catalysis*, 18 (1970) 329.
4 A. Lycourghiotis, *React. Kinet. Catal. Lett.*, 4 (1976) 453.
5 G. Pudberg and J. M. Smith, *J. Catalysis*, 12 (1968) 172.