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REVERSED-FLOW GAS CHROMATOGRAPHIC TECHNIQUE APPLIED TO MEASUREMENT OF MASS TRANSFER COEFFICIENTS OF *n*-HYDROCARBONS ON PORAPAK P

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SUMMARY

The reversed-flow gas chromatographic technique has been used to measure mass transfer coefficients of *n*-hexane, *n*-heptane, and *n*-octane on a Porapak P solid sorbent. The values found correspond not to infinite solute dilution but to finite solute concentrations (non-linear chromatography). The results show that mass transfer in the porous polymer is mainly governed by surface diffusion. The increase of the C coefficients for *n*-heptane with temperature is due to a decrease in the partition ratio k value. Some results for *n*-heptane and *n*-octane are in good agreement with literature values found by infinite dilution methods.

INTRODUCTION

Mass transfer phenomena play an important role in gas chromatography (GC), not only from the analytical point of view[1], but also with respect to physicochemical measurements[2]. Virtually all mass transfer studies in GC were made at infinite solute dilution by using conventional elution of an injected pulse. No mass transfer coefficient measurements at finite solute concentration (non-linear region of chromatography) have come to our attention. These would obviously require the use of some kind of frontal analysis, displacement development or special equipment for finite concentration work. However, a new technique, termed reversed-flow gas chromatography (RFGC), requires only a slight modification of a conventional gas chromatograph, and can lend itself to mass transfer measurements *at finite concentration,* by means of elution bands like those obtained with trace amounts of solute.

The RFGC technique has been successfully used to determine diffusion coefficients in binary and ternary gas mixtures[3,4], together with their temperature variation[5], adsorption equilibrium constants[6], rates of drying in solids[7], rate coefficients for evaporation of liquids[8], rate constants, activation parameters and catalytic conversions of surface-catalysed reactions[9–16], relative molar responses of the thermal conductivity detector and from these molecular diameters and critical volumes of gases[17], and finally Lennard-Jones parameters[18]. The method has recently been reviewed[19].

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For the present application of RFGC a porous polymer (Porapak P) was chosen, because such materials are widely used as sorbent phases in gas–solid chromatography, and also because relatively few quantitative data on solute mass transfer in gas–solid systems are available. An additional reason for this study was that similar measurements on porous polymers at infinite dilution by Rakshieva *et al.*[20] and Guha *et al.*[21] revealed that adsorption–desorption kinetics make a negligible contribution to the C coefficients found, and that surface diffusion controls the mass transfer phenomenon in the solid state. The possible role of surface diffusion in chromatography and the lack of relevant experimental data were pointed out by Giddings a long time ago[22].

EXPERIMENTAL

Materials

Porapak P was a product of Waters Assoc., U.S.A., Batch No 1995, 80–100 mesh. The carrier gas (helium) was obtained from Linde (Greece) and had a purity of ⩾99.99%. The solutes *n*-hexane and *n*-heptane were purchased from Merck (Uvasol, 99.9%), whereas *n*-octane was a product of Fluka (purum, 99.8%).

Apparatus

An experimental set-up similar to that used to measure gas diffusion coefficients[3] was used with a slight modification as shown in Fig. 1. An ordinary gas chromatograph (Pye Unicam 104) with a flame ionization detector contained in its oven two sections l and l' of a chromatographic column (39 + 39 cm × 4 mm I.D.) filled with Porapak P. The ends of this column D_1 and D_2 were connected to the carrier gas supply and the detector *via* a six-port valve S, so that when the valve was turned from one position to the other the direction of the carrier gas flow *was reversed.* A diffusion column L (80 cm × 4 mm I.D.), empty of any chromatographic material and with a U-shaped liquid reservoir at its upper end, was connected perpendicularly at its lower end to the middle of the filled column $l + l'$. The column L and the liquid reservoir were kept at a constant temperature in the range 48–62°C by means of water circulated around them from a thermostat.

Procedure

The conditioning of the chromatographic column $l + l'$ containing the Porapak P was carried out at 170°C for 24 h with a carrier gas flow-rate of 0.33 $cm^3 s^{-1}$. After that, the column was brought to each working temperature, and while carrier gas was flowing in a certain direction through the column $l + l'$, a small amount of liquid solute (usually 0.5 cm^3) was introduced by injection into the heated upper reservoir of column L. After a certain time, during which no signal was noted, an ascending concentration–time curve for the solute was recorded. This reached a maximum plateau and remained there as long as there was still liquid in the reservoir (see Fig. 4 in ref. 8). Thus, a finite solute concentration in the Porapak column was established, the magnitude of which depended on the vapour pressure of the liquid solute at the temperature of the reservoir. When sufficient stability of the recorded signal was attained, valve S was switched to the other position (broken lines), thereby *reversing* the direction of the carrier gas flow. After a short time interval t' (20–60 s) of back-

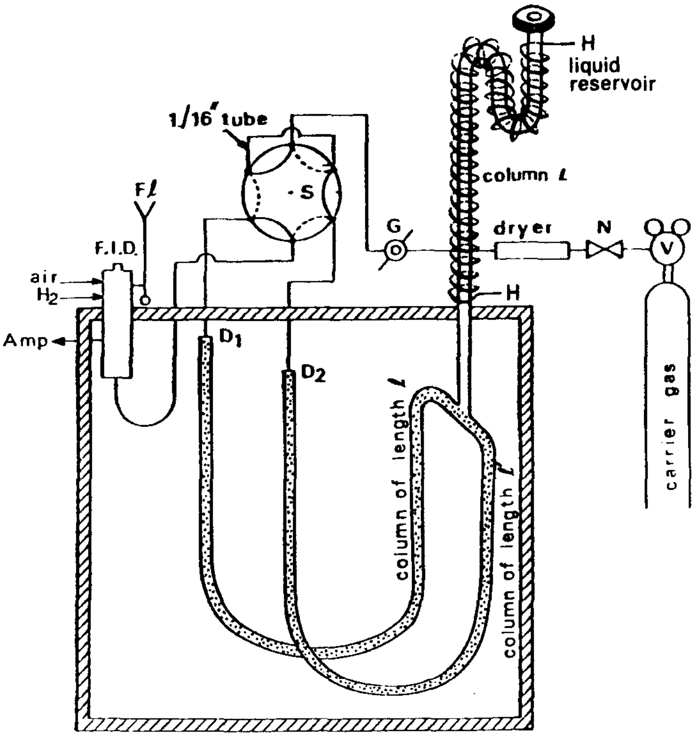

Fig. 1. Gas lines and connections for measuring mass transfer coefficients by RFGC: V = two-stage reducing valve and pressure regulator; N = needle valve; H = heating coil by water circulation; G = gas flow controller; S = six-port valve with a short 1/16-in. tube connecting two alternate ports; Fl = bubble flow-meter; Amp = signal to amplifier.

ward flow, the valve was turned back to its previous position, thus restoring the gas flow to its original direction.

Because the duration t' of backward flow was smaller than the retention time of the solute t_R and t'_R on column sections l and l', respectively, it created a perturbation in the concentration–time line with the form of a bell-shaped peak ("sample peak"). This emerged with a characteristic retention time after the restoration of the gas flow to its original direction, and "sited" on the otherwise finite concentration signal (*cf.* Fig. 2). The procedure was repeated several times, giving a series of sample peaks.

The pressure drop along column l or l' was found by measuring the pressure at the injection point of the solute with an open mercury manometer.

Experiments at 120, 135, 150 and 165°C were carried out with each solute, using time reversals t' of 20, 30, 40, 50 and 60 s.

Processing of the results

The mass transfer resistance coefficients C, together with the coefficients $\bar{B}$, were found by fitting the experimental data to the simple classical Van Deemter equation $\hat{H} = A + \bar{B}/\bar{v} + C\bar{v}$, using a least-squares program on a desk-top computer.

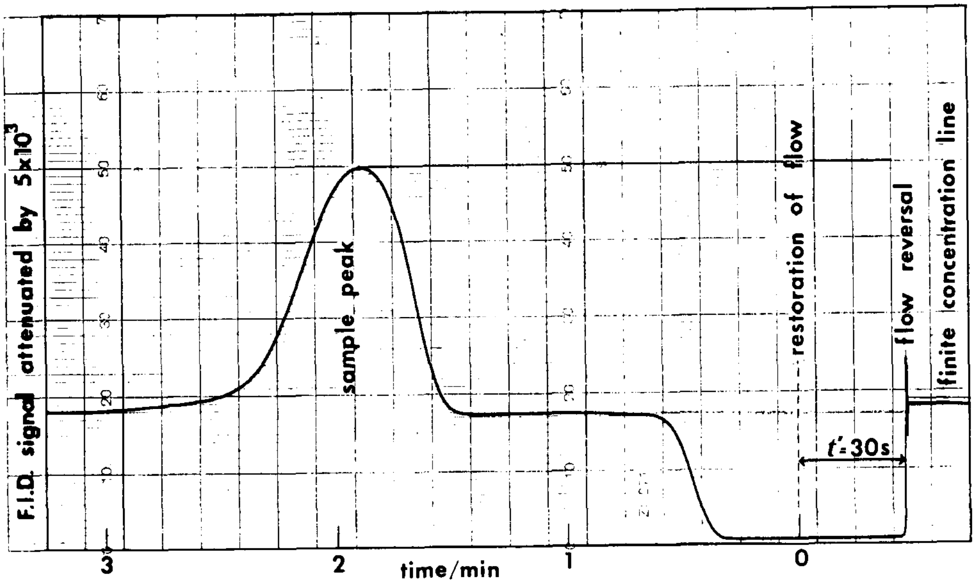

Fig. 2. A sample peak created by reversing the flow direction of carrier gas for 30 s while a finite concentration of *n*-heptane was passing through the column at 408 K, and a volumetric flow-rate of 1.07 cm^3s^{-1}.

The apparent (i.e. experimental) plate height $\hat{H}$ was calculated from the relation $\hat{H} = l/N$, and the number of theoretical plates N from the ratio t_R^2/σ_{net}^2, where t_R is the retention time of the sample peak, measured from the moment of the restoration of the flow to it original direction, and σ_{net}^2 is the net variance of the peak; these two parameters were computed as follows.

According to the theory of the RFGC method[5,19], the reversal of the flow for a time $t' < t_R$ creates a plug (*i.e.* a square function) on the continuous signal due to the diffusion of vapours from column L into column $l + l'$ (see Fig. 1). This square function has a theoretical width t', *i.e.* equal to the time of the backward flow, and its variance is therefore $t'^2/12$. When passed through the Porapak column section l or l', the sample peak will be given by the difference of two error functions[23]. Its variance σ_{exp}^2 and retention time t_R were calculated by the rectangular method of peak-area measurement introduced by Sternberg[24]. For each peak, 9–13 horizontal rectangles were used with 0.5–1-cm increments. In a few cases, where the peaks were of small height, the variance was calculated from the relation[2]

$$\sigma_{exp}^2 = \frac{1}{4}(t_+ - t_-)^2$$

where t_+ and t_- are the times corresponding to the inflection points of the curve. Finally, the net variance due to the chromatographic process was found from the difference

$$\sigma_{net}^2 = \sigma_{exp}^2 - \frac{t'^2}{12} \qquad (1)$$

RESULTS AND DISCUSSION

Table I summarizes the results obtained as outlined in the previous section. As was pointed out in the Introduction, the present study is a plate height measurement at finite concentration. Therefore, before discussing the mass transfer term C, it is worth commenting on the values of the coefficients A and $\bar{B}$. The particle diameter for a 80–100 mesh solid material, such as that used here, is 0.018–0.015 cm and most of the A values in Table I are of that order of magnitude, as in most infinite dilution studies. The negative values are probably due to experimental errors, since the term A is very sensitive to these errors.

The diffusion coefficients D_m of the solute vapours in the carrier gas helium were calculated, at each column temperature from the Fuller–Schettler–Giddings equation[25]. These values (given in Table I for 1 atm pressure) were used to find the obstruction factor γ from the well-known relation $\bar{B} = 2\gamma D_m$. In this calculation, each D_m value was first reduced to the mean column pressure, corresponding to the mean flow velocity of the carrier gas. The γ values found, listed in the last column of Table I, seem reasonable.

Coming now to the C coefficients, we first note that they do not include a mobile phase diffusion term C_m, since they are independent of pressure. There are three main points to be discussed: (1) the magnitude of C terms; (2) their variation with t', *i.e.* with the width of the square function created by the flow reversal; and (3) their variation with temperature.

(1) The C coefficients found are too large to be attributed to adsorption–desorption kinetics, *i.e.* being $C_k = 2k/(1+k)^2 k_d$, where k is the partition ratio and k_d is the desorption rate constant. The C_k terms are of the order of 10^{-8} to 10^{-6} s, and therefore their contribution to the magnitude of C found must be negligible. This has also been pointed out by Rakshieva *et al.*[20], who studied the mass transfer coefficients of *n*-heptane on several kinds of Porapak, at 170°C. Their value of C_s for Porapak P-411 is 0.076 s, and this agrees with our values at the same temperature ranging from 0.028 to 0.089 s (*cf.* Table I). Also our value of C (0.011 s) for *n*-octane at 170°C agrees with the C_s (0.008 s) found by Guha *et al.*[21] under similar conditions.

TABLE I

VALUES FOR THE COEFFICIENTS A, $\bar{B}$ AND C OF THE VAN DEEMTER EQUATION DETERMINED BY RFGC AT FINITE SOLUTE CONCENTRATION

Solute	*T(K)*	*t'(s)*	*A(cm)*	$\bar{B}$*(cm²s⁻¹)*	*10²C(s)*	D_m*(cm²s⁻¹)*	γ
n-Heptane	393	30	0.029	0.271	1.34	0.443	0.39
	393	60	−0.004	0.289	3.40	0.443	0.39
	408	20	0.058	0.253	1.40	0.462	0.32
	408	30	0.079	0.225	1.85	0.462	0.29
	408	40	−0.015	0.376	2.98	0.462	0.51
	423	20	–	–	2.76	–	–
	423	30	0.041	0.294	4.95	0.503	0.33
	423	40	−0.179	0.544	8.90	0.503	0.64
	438	30	0.002	0.264	5.40	0.535	0.29
n-Hexane	423	30	−0.139	0.410	9.80	0.515	0.49
n-Octane	423	30	–	–	1.15	–	–

We can therefore adopt the explanation given by the above authors[20,21], that it is surface diffusion that controls the mass transfer of solute in the solid phase.

(2) Table I shows that there is a 2.1 to 3.2 fold increase of C when t' is doubled. This can be explained by referring to the finite solute concentration, on account of which the isotherm may not be linear. A decrease in the isotherm slope brought about by an increase in t' will cause a decrease in k. Since C is usually of the form[26]

$$C = N\frac{k}{(1+k)^2 D_{\text{eff}}} \tag{2}$$

where N is a constant and D_{eff} is an effective diffusion coefficient pertaining to the appropriate mass transfer mechanism, C will increase with decreasing k (provided that $k > 1$) and hence with increasing t'.

(3) The variation of C with temperature at constant t' (30 s) is shown in Fig. 3 in the form of a plot of ln C *versus* $1/T$. It shows an increase of C with temperature, and this is an unusual dependence, at least for infinite dilution studies. For instance, Guha *et al.*[21] found a small decrease of C_s with increasing T for *n*-octane on Porapak P, whereas for iso-octane the decrease was large, corresponding to an activation energy of 73.6 kJ mol^{-1} for diffusion into the micropores of the polymer. *n*-Octane, on the other hand, was assumed to have almost free access into the pores. If this argument applies also to *n*-heptane, the variation of D_{eff} of eqn. 2 with temperature cannot be responsible for our C dependence on T, not only because of the small magnitude of the activation energy expected, but also because it is in the opposite

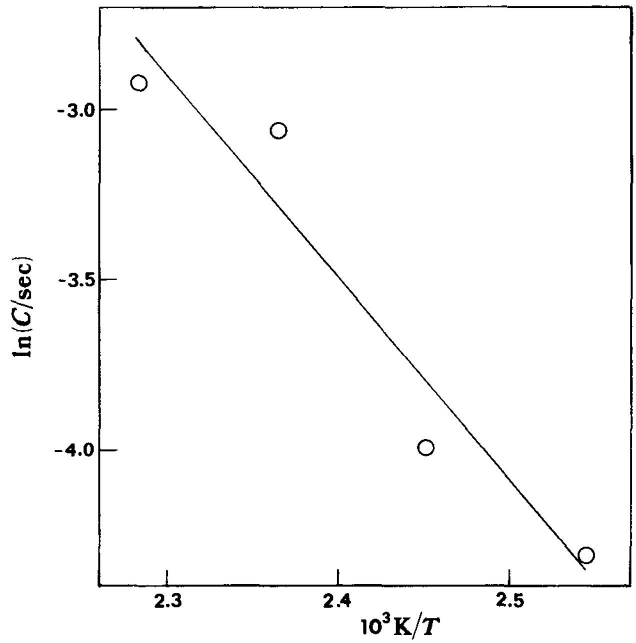

Fig. 3. Temperature dependence of C for *n*-heptane on a Porapak P column.

direction. An obvious explanation for the behaviour of C in the present case lies on the decrease of k with temperature. For $k \gg 1$, eqn. 2 becomes

$$C \simeq \frac{N}{kD_{\text{eff}}} = \frac{N'}{KD_{\text{eff}}} = N''\exp\left[(\Delta H_{\text{ad}} + E)/RT\right] \tag{3}$$

where N' and N'' are constants, k is the adsorption equilibrium constant, ΔH_{ad} the heat of adsorption and E the activation energy of D_{eff}. According to this equation, a plot of ln C *versus* $1/T$ should be linear with a slope equal to $(\Delta H_{\text{ad}} + E)/R$. From Fig. 3 we find a slope of $-5.931 \cdot 10^3$ and this gives $\Delta H_{\text{ad}} + E = -49.3$ kJ mol^{-1}. The heat of vaporization for *n*-heptane at its normal boiling point (98.4°C) is 31.7 kJ mol^{-1}, and if we take $E = 0$, because of the small activation energy expected (*cf.* above), the heat of adsorption is only 1.6 times bigger than the heat of vaporization. This places the adsorption of *n*-heptane on Porapak P in the domain of physical adsorption. For comparison we quote here the heat of adsorption of *n*-heptane on graphitized carbon black, equal to -52.3 kJ mol^{-1}.

CONCLUSION

The RFGC technique can be employed for mass transfer coefficient studies at finite solute concentrations, with only a slight modification of an ordinary gas chromatograph. In spite of finite concentrations (non-linear chromatography), the method is based on simple elution of extra peaks created on the existing finite solute concentration.

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