iGC SEA
Application
Note 201

Gas phase diffusion studies of cyclohexane by infinite dilution inverse gas chromatography

Surface Measurement Systems Ltd

The shape of experimentally obtained IGC peaks is influenced by gas phase diffusion effects becoming stronger at smaller flow rates. At very high flow rates the assumption of equilibrium is no longer valid and adsorption will be less than in the equilibrium state. This paper shows a way to find the best compromise between both influences. Elution studies were done on α-Lactose-Monohydrate with cyclohexane in the infinite dilution range

---

Introduction

A common dynamic sorption method is inverse gas chromatography (IGC) [1].IGC involves the sorption of a known vapour (adsorbate, probe molecule) on an unknown adsorbent stationary phase (solid sample). This approach inverts the conventional relationship between mobile and stationary phases found in analytical gas-solid chromatography.

Generally IGC measurements can be done in two ways: with a pulse technique or as a continuous, usually frontal experiment. In a pulse measurement an injection of a certain amount of an adsorbate is made. This pulse is transported by a carrier gas, helium for this study, through the column and adsorbs on the solid sample. The adsorbed vapour is eluted by the carrier gas.

IGC may be experimentally configured for infinite dilution or finite concentrations of the vapour. The first method is excellent for the determination of surface energies and heat of sorption whereas at finite concentrations it is possible to measure adsorption isotherms for the determination of surface area and porosity [2]. The application of both approaches will be shown in further application notes.

Theory

In gas-solid adsorption chromatography the peak shape of a pulse, passing through a material (adsorbent), is affected by two effects: adsorption and diffusion.

In the infinite dilution range, at very low partial pressures of the vapour (adsorbate), the adsorption process is independent of the surface coverage of adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In the case of finite concentrations these assumptions are no longer valid and the adsorption isotherm becomes non-linear. This behaviour results in a skewed peak. In Figure 1 examples are shown for both cases [3].

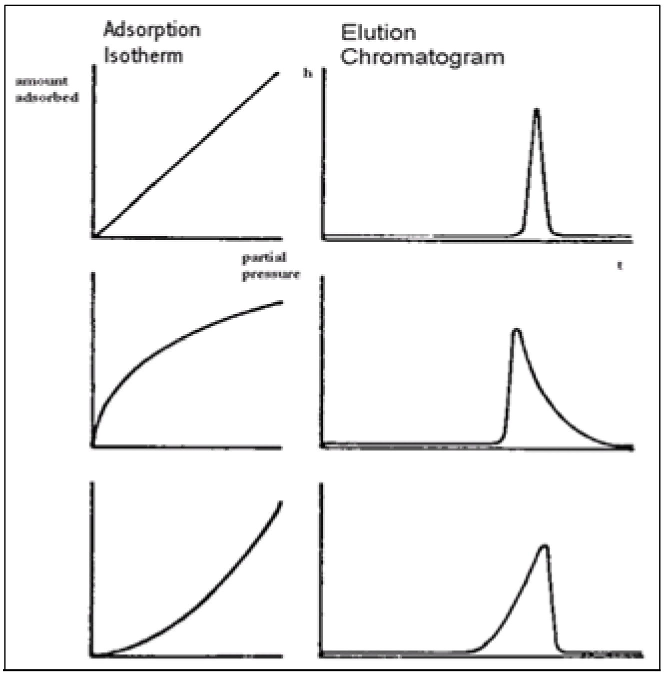

Figure 1. Correlation of peak form and sorption isotherm for finite and infinite concentration (illustration from [3]).

Nevertheless, the gas phase diffusion has a significant influence on the peak shape even at infinite dilution. Figure 2 illustrates different varieties of diffusion effects.

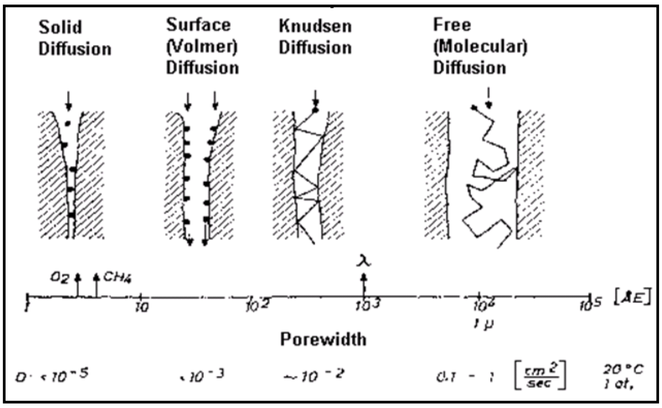

Figure 2. Different diffusion types for gas-solid chromatography (illustration from [4]).

Assuming the mean free path of the adsorbate is bigger than the width of any existing pore structure of the adsorbent the diffusion is dominated by longitudinal diffusion in the gas phase. Longitudinal diffusion can be separated into two contributions: the free or molecular diffusion and the eddy diffusion [4]. The molecular diffusion reflects the fact that the column has a particular length and diameter. Therefore the molecules spread in both axial and longitudinal directions. The eddy diffusion is due to the inhomogeneous particle shape or packing of the particles in the column. Therefore the velocity of molecules through the column varies. Both effects cause a broadening of the peak. Although this broadening apparently does not affect the analysis of an infinite dilution measurement it aggravates the results of finite concentration experiments and the detection of other diffusion effects such as bulk or pore diffusion. Moreover it increases the uncertainty of a statistical analysis such as a centre of mass calculation at infinite dilution. Therefore the flow rate becomes an important experimental parameter because the gas phase diffusion has a bigger impact with decreasing flow rate.

On the other hand the assumption of adsorption equilibrium for a pulse experiment is only valid at low flow rates because of the finite equilibrium times in a real system.

A good theoretical treatment can be made by the van Deemter equation (Equation 1) [1] which was developed for analytical chromatography but provides a reasonable description of the above mentioned effects in the case of IGC as well.

$$H = A + B / u + C \cdot u \qquad (1),$$

where H is the theoretical plate height, u the linear flow rate and A, B and C constants. A represents the eddy diffusion and is therefore related to the homogeneity of the column packing (Equation 2):

$$A = 2 \cdot \lambda \cdot d \qquad (2),$$

where d is the particle diameter and λ the factor that describes the statistical irregularity. The constant B represents the molecular diffusion and C is a measure for the equilibrium times and can be related to non-equilibrium effects such as bulk or pore diffusion [2].

Because the van Deemter equation takes all these effects into consideration it can be used to reveal optimum experimental conditions. A plot of the theoretical plate height H versus the linear flow rate u should show a minimum in the curve for the optimum flow rate.

The linear flow rate is calculated from the length L of the packed column bed and the dead retention time t_0 (Equation 3). The latter represents the time a non-adsorbing molecule needs to pass through the column.

$$u = L / t_0 \qquad (3).$$

The theoretical plate height can be derived from the bed length L, the half width b and the gross retention time t_R (Equation 4).

$$H = \frac{L}{8 \cdot \ln 2} \cdot \left(\frac{b}{t_R} \right)^2 \qquad (4).$$

The gross retention time represents the absolute time a molecule needs to reach the detector. The net retention time is therefore the difference between this and the dead time (Equation 5):

$$t_N = t_R - t_0 \qquad (5).$$

The minimum, which represents the optimum linear flow rate, can be obtained from the constants *B* and *C* (equation 6).

$$u_{min} = \sqrt{\frac{B}{C}} \qquad (6).$$

The constants can be derived from a fit of the van Deemter equation to the experimental curve. This calculation is provided by the SMS-*i*GC Analysis Macro Suite v1.1 Advanced.

Method

Six different columns were packed with α-Lactose-Monohydrate, supplied by Acros. The columns had internal diameters of 2, 3 and 4 mm and lengths of 170 and 340 mm to check the influence of column geometry. The amount of sample was 320 mg in all columns. All sorption experiments were carried out using the SMS-*i*GC. Measurements were done with cyclohexane at 303 K without any pre-treatment other than to equilibrate under the experimental conditions. For dead-time measurements methane was used. Cyclohexane experiments were carried out with four different concentrations p/po = 0.05, 0.1, 0.3 and 0.5 (loop size 0.25 ml). Flow rates used were between 5 and 25 ml/min.

Another experiment was done with the same amount of Lactose but using the SMS standard column (300 mm length and 2 mm diameter). The flow rate variation here was done between 5 and 35 ml/min.

All computed retention times are average values of at least 3 injections.

Results

Figure 3 shows the obtained peaks at different flow rates for an experiment with the standard column. As expected peaks of same injection size become narrower and higher with increasing flow rate. Moreover the retention times shift to smaller values.

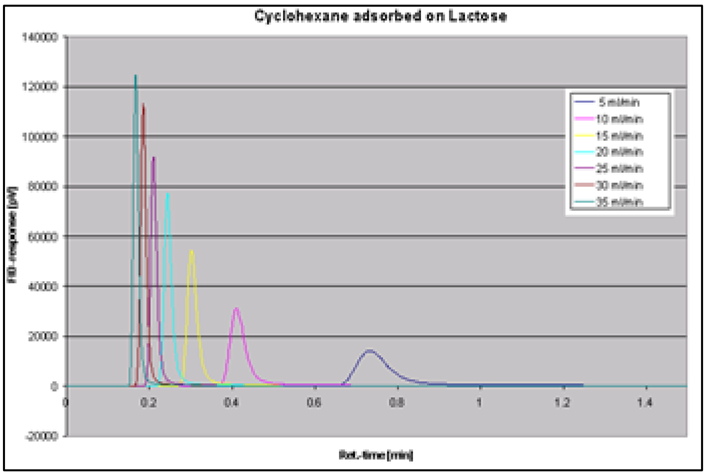

Figure 3. Variation of flow rate for cyclohexane (p/po = 0.05) on Lactose at 303 K.

The bed length was 17.4 cm, plate heights and linear flow rates are shown in Table 1.

Table 1. Experimental Data.

Flow rate (cm/min)	Plate height (mm)
24.126	0.4388
43.187	0.3471
59.063	0.3130
72.440	0.2761
84.630	0.2798
95.657	0.3278
106.552	0.3145

The plot of the results and the van Deemter fit is shown in Figure 4. The derived constants are: A = 12.0177 cm, B = 718.861 cm2/sec and C = 0.105 sec.

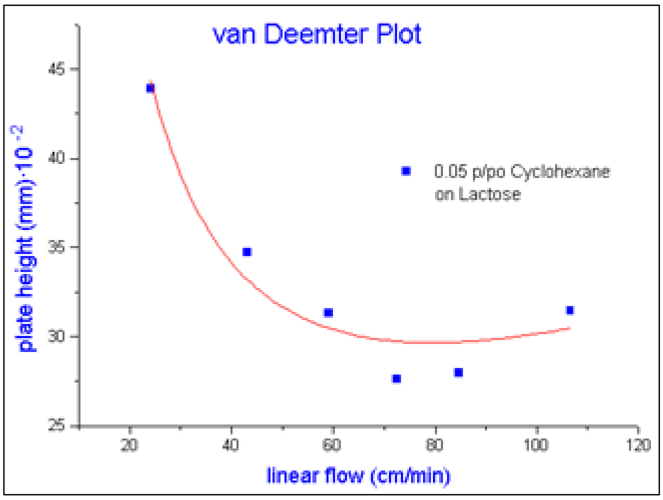

Figure 4. Van Deemter plot for 5 % cyclohexane on Lactose at 303 K.

Using Equation 6 an optimum linear flow rate of 82.66 cm/min results. This corresponds to a volume flow rate of 24.4 ml/min.

To investigate the dependence of optimum flow rate on column geometry a series of experiments have been carried out in the way described above.

All peaks showed a typical gaussian form (Figure 3). Therefore results should be similar at the different concentrations used in each experiment. This is also indicated by Figure 5 which shows similar van Deemter curves for a long 4 mm column.

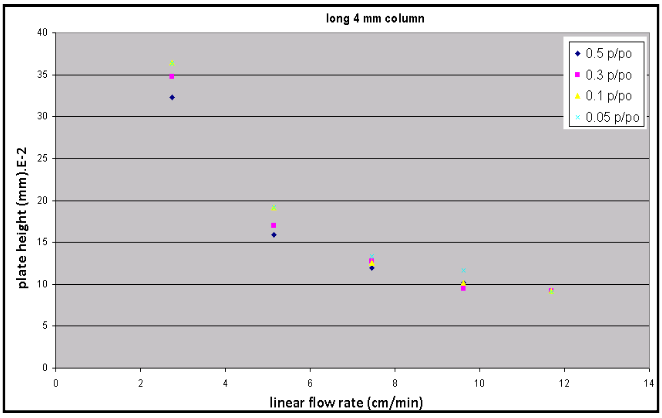

Figure 5. Van Deemter plot for different concentrations from an experiment with long 4 mm column.

Values obtained with 5 % cyclohexane have been used for a van Deemter fit. The results are illustrated in Table 2.

Table 2. Dependence of minimum flow rate from column length and diameter.

Column geometry	Min. flow rate (cm/min)	Min. flow rate (ml/min)
2 mm, long	21.51	21.7
3 mm, long	23.91	24.5
4 mm, long	14.02	29.2
2 mm, short	29.21	22.0
3 mm, short	34.16	27.4
4 mm, short	14.88	28.3

The change in diameter affects the results significantly. With increasing diameter the minimum flow shifts to higher flow rates. This can be explained by the gas phase diffusion that becomes larger in the same way. The length seems to have little influence although the variation for the 3 mm columns is larger. This difference is caused by the uncertainty of the fit based on only five different flow rates. For operators measuring on their own system it is recommended to use the maximum number of points provided by the control software.

This is also important in the recalculation of the minimum volume flow rate from the minimum linear flow rate. This can be done using Equation 7:

$$F = u \cdot t_m \cdot F_1 / L \qquad (7),$$

where F_1 is the volume flow rate close to the minimum.

Conclusion

The van Deemter equation can be used to optimise experimental flow conditions for a particular adsorbate-adsorbent system. Moreover the obtained constants contain information about homogeneity or non-equilibrium effects such as bulk sorption.

Acknowledgement:

Surface Measurement Systems thank Frank Thielmann and David Butler for their contributions to the application note.

References

---

[1] Williams, D.R., "Inverse Gas Chromatography", in Characterisation of Composite Materials (Ed. H. Ishida), Butterworth, pp.80-103, 1994
[2]Kiselev, A.V. and Yashin, Y.I., Gas-Adsorption Chromatography, Plenum Press, 1969
[3]Schwedt, G., Chromatographic Separation Methods, Thieme, 1994
[ ]Peters, W, and Jüntgen, H., Brennstoff-Chemie 46 (1965), 56
[4]van Deemter, J., Zuiderweg, F.J. and Klinkenberg, A., Chem. Eng. Sci. 5 (1956), 271
[5]Habgood, H.W. and Hanlan, J.F., Can. J. Chem.. 37 (1959), 843