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INVESTIGATION OF ADSORPTION EQUILIBRIUM IN CHROMATOGRAPHIC COLUMNS BY THE FRONTAL METHOD

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SUMMARY

   Methods for measuring adsorption isotherms from solutions are described and compared. On the basis of a comparison of asdsorption isotherms measured by dynamic and static methods, an equation describing the equilibrium conditions in liquid chromatography is suggested. A method for determining the void volume of chromatographic systems based on the thermodynamics of adsorption was developed.

INTRODUCTION

   The question of the attainment of dynamic equilibrium in the adsorption process in a chromatographic column is of great importance as it defines the accuracy and reproducibility of chromatographic results in analytical applications and also in physico-chemical studies of adsorption systems. Various aspects of this problem have been investigated[1,2]. Independence of the retention volume from the flow-rate of the mobile phase is assumed to be one of the basic criteria of adsorption equilibrium in chromatographic processes: the retention volume must not depend on flow-rate when the chromatographic column is in the equilibrium with the mobile phase. However, various steric and other factors may influence the thermodynamic equilibrium in the column. We can conclude that equilibrium in the column is achieved when the isotherm measured by the static method coincides with that measured by the frontal method.
   Many papers have dealt with the measurement of the adsorption isotherms of various compounds by liquid chromatographic methods[3–5]. The well known method of frontal chromatography showed the thermodynamic basis of this method for the measurement of the isotherms of adsorption from solutions[4]. Some workers used the (step-by-step) differential frontal method, the basic equation of which has been given by DeVault[6] and Whilson[7]. When adsorption is calculated by this method, all previous concentration points need to be taken into account, but this leads to an accumulation of errors. Therefore, it is necessary to determine the void volume of the chromatographic column very precisely.
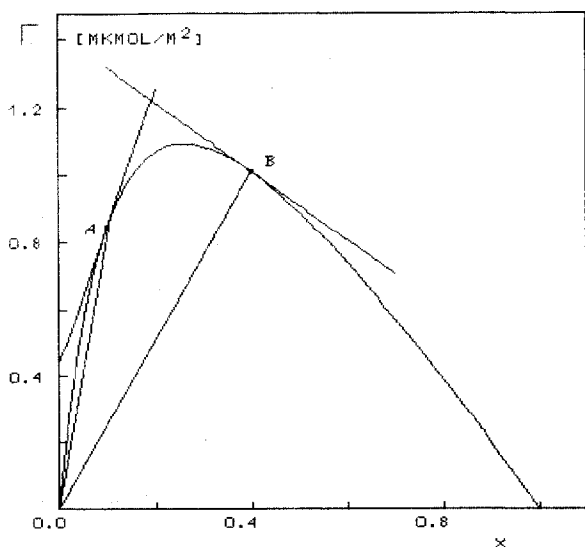
Fig. 1. Principle of the determination of adsorption isotherms by the whole frontal method (the retention time is proportional to the slopes of the lines from the origin to the points A and B, and by the differential method (the retention time is proportional to the slopes of the tangents to these points.

THEORY

We propose the use of eqn. 1, involving the measurement of the slope of the tangent to the adsorption isotherm based on experimental concentration points (Fig. 1):

$$u = \frac{w}{1 + \dfrac{S}{V} \cdot \dfrac{d\Gamma}{dc}} \tag{1}$$

where w is the flow-rate of the mobile phase, u is the velocity of movement of the investigated concentration point, S is the surface area of the stationary phase, V is the volume of the mobile phase in the column and $d\Gamma/dc$ is the differential of the isotherm at a given concentration point.

The retention time of the front from pure eluent to the chosen concentration point A (or B) in Fig. 1 will be proportional to the slope of the straight line from 0.0 to A (or B). This method has the advantage that in each experiment we measure directly one point on the adsorption isotherm independently on the other experiments and the measurement of the void volume may be carried out on the same system. In this event, eqn. 1 will be in the form

$$V_r = V_0 + mS \cdot \frac{\Delta\Gamma}{\Delta c} \tag{2}$$

where V_{r0} is the void volume of the column and V is the retention volume of the compound investigated. It can be seen from Fig. 1 that when we measured the retention time (or volume) of the pure second component from the pure first compo-
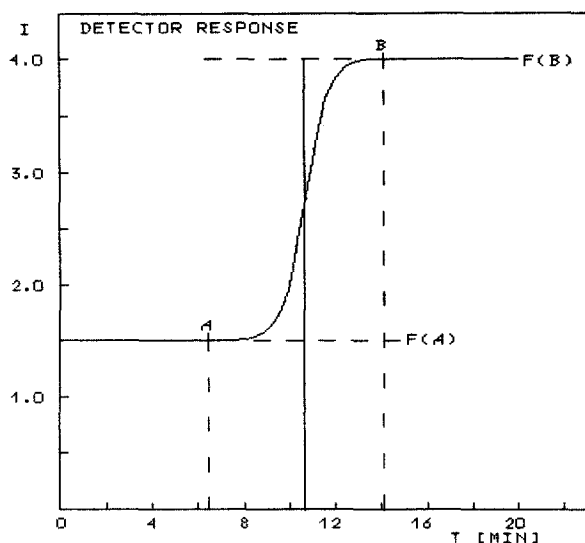
Fig. 2. Chromatogram for the whole frontal method.

nent, the line will be phase through abscissa and the measured retention volume (from eqn. 2) will be equal to the void volume of the chromatographic system. One of the main advantages of the proposed method is the independence of the retention volumes of the middle mass points of the front from the kinetic and thermodynamic broadening of the front, as shown in Fig. 2 and by eqn. 3

$$t = B - \frac{\int_A^B f(t) \, dt}{f(b) - f(a)} \tag{3}$$

where t is time, A and B are the integration limits which must be chosen freely on the concentration plateaus (not on the front) and f (a) and f (b) are the values of detector response at points A and B, respectively.

According to the equation of mass balance, the movement of the point chosen by eqn. 3 was determined only by the value of the adsorption isotherm at that point, corresponding to the concentration of the injected solution.

EXPERIMENTAL

The automatic chromatographic system shown in Fig. 3 was designed for measuring adsorption isotherms by total frontal and differential frontal methods. This system allows measurements to be made by both methods on the same chromatographic system, conversion from one to the other being carried out simply by changing the computer program.

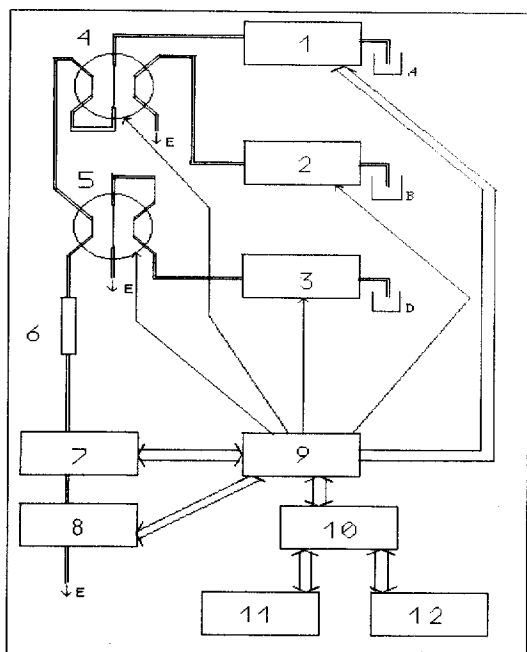When measuring an isotherm by the differential method pump 1 is pumping

Fig. 3. Scheme of experimental system designed for frontal chromatography: 1, 2, 3 = pumps; 4, 5 = valves; 6 = column; 7 = detector; 8 = flow meter; 9 = interface; 10 = computer; 11 = plotter; 12 = display. A, B and D are reservoirs with the eluent with the eluent and the solutions, E is the outlet of the eluate.

the eluent, pumps 2 and 3 are pumping the solutions of the investigated compound by increasing (or decreasing) the concentration in the loop of the corresponding valves 4 and 5. When displacing a solution of certain concentration from the loop of valve 4, simultaneously the loop of valve 5 is filled with solution of the next concentration from pump 3. When the equilibrium concentration appeares in the detector, the computer turns valves 4 and 5 simultaneously and stops pump 3. Also, the computer activates pump 2 to fill the loop of valve 4 with the solution of the investigated compound with the next concentration. At that time pump 1 displaces the solution from loop 5 to the column. This system allows the total isotherm to be measured under automatic condition. Measurements are carried out by increasing or by decreasing the concentration, which allows an additional check to be made of equilibrium and the whole desorption (the retention times of the middle mass points when passing the isotherm forwards and backwards must concide).

The total frontal method can be applied when using only two pumps and one valve in the same chromatographic system. In this instance pump 1 is pumping the pure eluent through the column and pump 2 is filling the loop of valve 4 with solutions of various concentrations; valve 5 always is in the "probe injection" position and hence pump 5 is always shut off.

The equilibrium investigations were carried out on the system benzene–n-heptane–hydroxylated silica gels with various flow-rates of the mobile phase using silica gels with various surface areas and pore diameters (Table I). Comparisons of the measured adsorption isotherms with static experimental data were made[8].

TABLE I

PROPERTIES OF SILICA WITH HYDROXYLATED SURFACE USED

Silica	Specific surface area (m²/g)	Pore diameter (nm)	Particle diameter (μm)
KSS-3	520	7	15
KSK-2.5	380	10	10
KSK-2	340	14	10
S-1	120	30	10
S-80	85	55	15

RESULTS AND DISCUSSION

We determined the adsorption isotherms on the adsorbents listed in Table I for various eluent flow-rates by the frontal method. By comparing the adsorption isotherms we can find the statistical boundary of equilibrium (Fig. 4, straight line), which may be described by the equation

$$d(\text{nm}) = 100 \, (2.5 \pm 0.5) \, w(\text{cm/s}) - 8 \tag{4}$$

This equation may be used for the determination of the optimal conditions for a chromatographic separation under equilibrium conditions. For example, if we have a known adsorbent, we can find the flow-rate that will correspond to the equilibrium process and *vice versa*, if we wish to separate a mixture at the appointed time we can find the pore diameter of the adsorbent that corresponds to the equilibrium conditions.
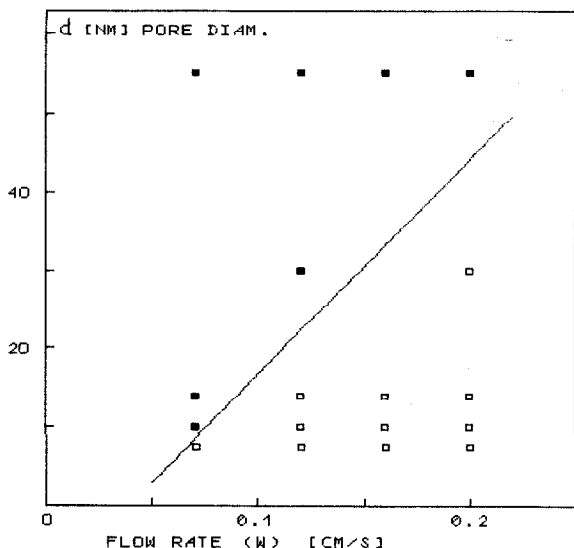

Fig. 4. Equilibrium criterion of chromatographic experiments on flow-rate and pore diameter of adsorbents: □, non-equilibrium experiments (isotherms measured by static and dynamic methods do not coincide); ■, equilibrium experiments.

The comparison of the differential and total frontal methods was carried out on the system acetonitrile–water–Separon-C_{18}. This interesting system had an azeotropic point on the adsorption isotherm which was shown approximately (with a model of the adsorption layer) in ref. 9.

The total frontal method allows the measurement of the adsorption isotherm without any assumption about the structure of the adsorption layer. Fig. 5 shows the dependence of the retention times of the middle mass points of the fronts on the injected equilibrium concentration for two methods, and also (Fig. 5C) the experimental adsorption isotherm of acetonitrile from aqueous solution on to the bonded stationary phase Separon-C_{18}. From a comparison of these curves it can be seen that the dependence of the retention time for the whole frontal method corresponds to the form of the adsorption isotherm, whereas that for the differential method corresponds to the derivative to the adsorption isotherm with respect to concentration, which is why we propose to term this method "differential" and not "step-by-step".

It is very important that the void volume can be determined from the dependence of the retention value defined by the differential method from the condition
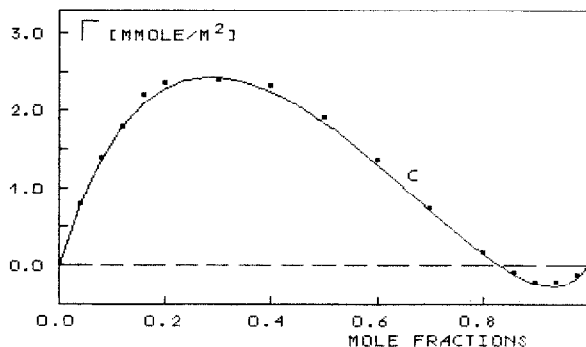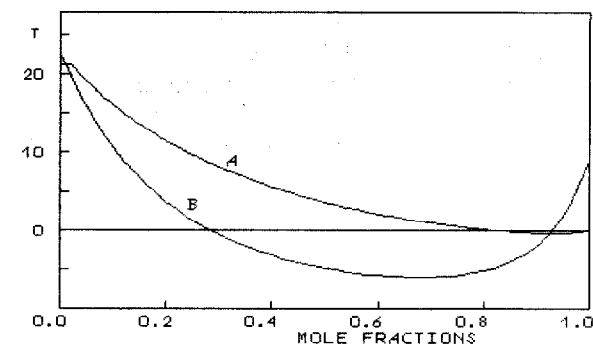
$$\int_0^1 [V_r(x) - V_0]\, dc = 0 \tag{5}$$

Fig. 5. Dependence of the retention time of fronts on the injected equilibrium concentration for the whole frontal frontal method (A) and for the differential method (B). (C) Isotherm of adsorption of acetonitrile from water on Separon-C_{18} measured by the whole frontal method.

because the excess isotherm of adsorption of a pure component was zero. On the basis of this conclusion, we propose a method for the determination of the void volume in the elution variant of chromatography.

If we have a detector sensitive to small changes in the composition of the mobile phase, we can define the retention time of the small disturbance peak that is moving along the column. The retention volume of this disturbance peak is determined by eqn. 2. This experiment may be carrying out by injection of a sample of eluent with a small differences from the composition used. One can use a refractive index or a UV detector, which has a clear response to small changes in absorbance from changes in the refractive index of the solution. On passing through the whole range of concentration from the pure first to the pure second eluent we can to calculate the void volume from eqn. 5. Because the excess isotherm of a pure component is zero, the integral of the difference in retention volume and void volume over the whole concentration range must be zero.

Now we can calculate the value of the void volume of the chromatographic system by solving eqn. 5 with respect to V_0 of chromatographic system. It is important that this value has a thermodynamic basis and does not depend on the eluent composition, as distinct from the dependences shown in the literature for the void volume determined by the retention time of the "unadsorbed" component.

It can be concluded on the basis of these data that the proposed method of measurement permits the isotherm of adsorption from solution to be determined more easily than previous methods. This method also permits the determination of the void volume, and has particular importance in the physico-chemical application of liquid chromatography, where the errors in the determination of void volumes have great importance with regard to calculated thermodynamic values.

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