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STUDY OF ADSORPTION FROM SOLUTIONS BY COLUMN CHROMATOGRAPHY*

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SUMMARY

A column chromatographic method is proposed for obtaining data on equilibrium characteristics of adsorption; the method makes it possible to obtain in a single chromatographic experiment the excess adsorption isotherm of binary solution over the whole range of concentrations. The potentials and limitations of the method with respect to equilibrium data and thermodynamic characteristics of adsorption systems are discussed. A comparison with static experimental data is made.

INTRODUCTION

The development of industrial separation and purification processes requires data on equilibrium partition coefficients and adsorption kinetics. The information on partition coefficients is usually obtained by measuring static adsorption isotherms of mixtures to be separated. This method has a number of advantages but is very time consuming. In equilibrium chromatography, elution curves provide information about adsorption isotherms^{1,2}. Therefore, some workers have used chromatography for the determination of adsorption isotherms of gases and vapours³⁻¹⁰. In connection with progress in high-performance liquid chromatography (HPLC) the method has been applied to adsorption from liquid mixtures¹¹⁻¹⁴. This paper deals with the potential of the method.

THEORETICAL

The method is based on the well known equation of concentration point movement:

$$\left(-\frac{\partial x}{\partial V}\right) = \frac{1}{m\alpha + \Gamma(x)} \quad (1)$$

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where x is the distance covered by a concentration point φ when the eluent (volume V) passes through the column, m is the mass of an adsorbent in the column, f is the first derivative of the adsorption isotherm at the point with equilibrium concentration φ and α is the free volume of the column.

From eqn. 1 we can obtain an expression for the calculation of adsorption at the point with concentration φ :

$$f(\varphi) = \frac{1}{m} \int_0^{\varphi} (V\varphi - \alpha) d\varphi \quad (2)$$

Thus, knowing only the elution curve for the separation of component A from component B it is in principle possible to calculate the adsorption isotherm of the binary mixture A-B over the entire range of concentrations.

However, the use of eqn. 2 raises a number of problems:

(1) Two types of adsorption isotherm can be distinguished when studying adsorption of solutions by the static method: a surface excess isotherm and an absolute content adsorption isotherm. The surface excess, n_1^s , can be found directly from an adsorption experiment if the initial and the equilibrium concentrations of the solution, the mass of the adsorbent and the amount of the solution are known:

$$n_1^s = \frac{n^0 \Delta x_1}{m} \quad (3)$$

where n^0 is the amount of the substance in the solution, m is the mass of the adsorbent and Δx_1 is the change in concentration of the solution due to adsorption. The absolute content of the substance in the adsorption solution, n_1^c , is related to the surface excess as follows:

$$n_1^c = n_1^s + (n_1^s + n_2^s) x_1 \quad (4)$$

To take advantage of this expression, an additional relationship, $n_1^s = f(n_2^s)$, should be known. The questions arise of the derivative of which adsorption isotherm is to be used in eqn. 1 and the type of adsorption that is measured in the chromatographic experiment. These questions were first considered in refs. 15 and 16, where it was shown that $f(\varphi)$ in eqn. 2 is the surface excess isotherm and α is the free volume of the column, including the volume of the adsorbent pores. Thus, it is the surface excess that is determined in the chromatographic experiment, just as in static measurements.

(2) Eqn. 1 has been derived for the equilibrium adsorption on the assumption that the broadening effects due to diffusion and mass transfer are absent. To what extent is this assumption justified? It is known from experience in and the theory of liquid chromatography that to meet these conditions it is necessary to use micron-sized particles, suitable methods for column packing, optimal flow-rates and special experimental units that reduce the extra-column broadening to a minimum. It should be noted that it is not always possible to meet the first two conditions.

(3) With steep adsorption isotherms (strong specific interactions), the amount adsorbed is already large at low concentrations and, as can be seen from eqn. 1, the

elution time may be very long for small concentrations. Also, the tail of the elution curve is too long, and therefore large amounts of solvents and long times are required for elution; finally, to reduce errors of integration of eqn. 2 it is necessary to detect accurately very low concentrations, which substantially limits the potential of the method.

EXPERIMENTAL

Surface excess isotherms were obtained at 303°K by a chromatographic procedure described previously¹³. All measurements were carried out on AC charcoal (Barnebey Cheney, U.S.A.) with Dubinin's parameters $W_0 = 0.38$ and $B_{\text{benzene}} = 0.75 \cdot 10^{-6}$ (where W_0 is the volume of the adsorption space, *i.e.*, the micropore volume, and B is the basic structure characteristic of the porous structure of the adsorbent¹⁸), and with volumes of micropores, mesopores and macropores of 0.38, 0.04 and 0.17 cm³/g, respectively. The components of the binary solutions were benzene, 2,2,4-trimethylpentane, ethanol and carbon tetrachloride (all analytical-reagent grade).

RESULTS AND DISCUSSION

We carried out experiments to test the limits of the application of the method as regards adsorption isotherm measurements^{13,14}. It has been shown that for systems with zero excess adsorption it is virtually impossible to avoid broadening of the elution curves because of the finite time of diffusion and mass transfer. As a result, the surface excess quantity, calculated from the elution curve, is not zero for systems that exhibit zero adsorption excess in the static experiment. This leads to elevated values of adsorption from eqn. 2. In particular, appreciable errors arise for systems of low selectivity.

Fig. 1 shows adsorption isotherms obtained from the elution curve with no account being taken of the broadening effects. It can be seen that for the system carbon tetrachloride–isooctane the surface excess amount obtained in the dynamic experiment exceeds the value from the static experiments by about 30%. Thus, a

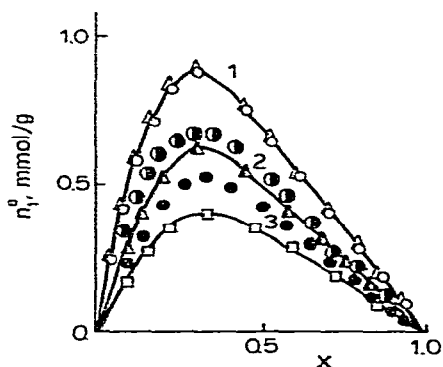


Fig. 1. Surface excess isotherm for the systems (1) benzene–isooctane on silica gel, (2) benzene–carbon tetrachloride on silica gel and (3) carbon tetrachloride–isooctane on silica gel. O, ⊙, ⊚, No broadening taken into account; Δ, ▲, □, broadening taken into account.

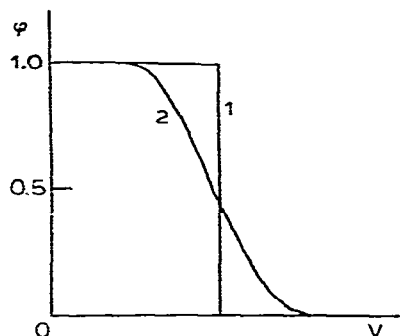


Fig. 2. Elution curve in ideal chromatography for (1) $\chi_{(\varphi)}^{(s)} = 0$ and (2) $\chi_{(\varphi)}^{(s)} > 0$, where χ is excess adsorption in ml/g.

correction for elution curve broadening is necessary in order to obtain a correct adsorption value.

The theoretical allowance for the band broadening processes requires a knowledge of a great number of physico-chemical parameters of the system, and in most instances this requires additional independent measurements. Again, one cannot evaluate the contribution of extra-column effects to the broadening, the effects being a characteristic of the liquid chromatographic (LC) system used. Therefore, an attempt has been made to develop a sufficiently simple and convenient empirical method of allowing for elution curve broadening.

We proceeded from the fact that in the case of a zero excess adsorption isotherm the band broadening is due to all factors with the exception of the adsorption isotherm itself. Fig. 2 shows schematically the ideal chromatographic elution curves for both a zero adsorption isotherm (curve 1) and non-zero one (curve 2). A schematic representation of the same curves in a real chromatographic experiment is shown in Fig. 3.

From the mass balance conditions, the areas under curves 1 and 2 (ideal and real chromatography) must be the same. From eqn. 2, it follows that the adsorption isotherm can be calculated from an ideal chromatogram with the help of the expression

$$f(\varphi) = \frac{1}{m} \int_0^{\varphi} (V_2 - V_1) d\varphi \quad (5)$$

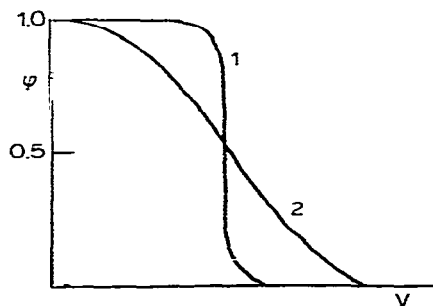


Fig. 3. Elution curve in non-ideal chromatography for (1) $\chi_{(\varphi)}^{(s)} = 0$ and (2) $\chi_{(\varphi)}^{(s)} > 0$.

We have assumed that the deformation of the elution curve due to the non-ideal chromatographic process should be the same both in the case of a zero adsorption isotherm and in the case of a non-zero one. Therefore, in non-ideal chromatography the elution volumes of appropriate concentrations obtained in a real chromatographic experiment for the system under study and for one where the excess adsorption is known to be zero should be introduced into eqn. 5. The criterion for zero adsorption is identity of the elution curves obtained when eluting component 1 by component 2 and *vice versa*. Fig. 1 shows the adsorption values (triangles) calculated with allowance for the broadening effects according to the above method. It can be seen that the dynamic adsorption data agree with the static data. The proposed correction method enabled us to use a very simple and cheap experimental unit and adsorbents with a particle size of 50–100 μm .

As has already been mentioned, another limitation of the method is that with steep isotherms very low concentrations have to be detected. Moreover, one can never be certain whether all of the substance has been eluted from the column. This gives rise to errors in the determination of adsorption. If a well designed LC system is available that ensures accurate volume measurements, this problem may be solved on the basis of mass balance computation. On the one hand, the volume of a substance in the column can be obtained by integrating the elution curve for the system with zero excess adsorption; on the other hand, the volume must be equal to that which is eluted in the case of a system with a non-zero excess adsorption. Equality of the volumes in both instances indicates complete elution of the substance from the column, and conversely, a difference indicates that the substance remains partially in the column. If the minimum concentration, φ_{min} , that can be adequately detected is known, then the amount of the non-desorbed substance corresponding to this concentration may be calculated from the relationship

$$\int_0^{\varphi_{\text{min}}} V_2 \, d\varphi = \int_0^1 V_1 \, d\varphi - \int_{\varphi_{\text{min}}}^1 V_2 \, d\varphi \tag{6}$$

However, in order to take advantage of eqn. 6, very accurate volume measurements are required and the experiments must be carried out carefully; otherwise, the discrepancy between the amounts of the substance eluted in the "zero" run and in the "main" run would be ascribed to the adsorption. In consequence, a serious error may be introduced in the result. Therefore, in practice it is convenient to take advantage of the following approach.

According to eqn. 5,

$$f(\varphi) = \frac{1}{m} \int_0^{\varphi} (V_2 - V_1) \, d\varphi$$

where V_1 and V_2 are true elution volumes. Let the elution curves $V'_i(\varphi)$ be measured. If the errors in V_2 and V_1 are ΔV_2 and ΔV_1 , respectively, then eqn. 5 can be written in the form

$$\frac{1}{m} \int_0^{\varphi} (V_2 - V_1) \, d\varphi = \frac{1}{m} \int_0^{\varphi} (V_2 - V_1) \, d\varphi + \frac{1}{m} \int_0^{\varphi} (\Delta V_2 - \Delta V_1) \, d\varphi \tag{7}$$

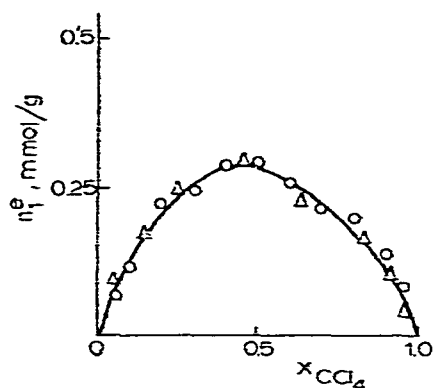


Fig. 4. Surface excess isotherm for the system carbon tetrachloride–isooctane on silica gel. O, Chromatographic method of measurement; Δ , static method of measurement¹⁷.

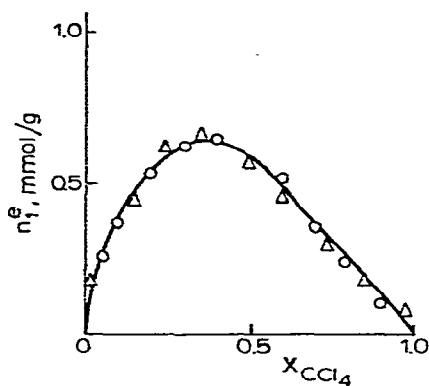


Fig. 5. Surface excess isotherm for the system carbon tetrachloride–isooctane on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

According to eqn. 5 the first integral of the right-hand side of eqn. 7 is the excess adsorption. When $\varphi = 1$, the excess adsorption is zero and we have

$$\frac{1}{m} \int_0^1 (V_2 - V_1) d\varphi = \frac{1}{m} \int_0^1 (\Delta V_2 - \Delta V_1) d\varphi \quad (8)$$

As practice has shown, the largest errors in V_2 and V_1 are introduced when the substance in the column is changed, *i.e.*, with the shapes of the elution curves in parallel runs coinciding, one can observe their relative displacement along the t axis. Therefore, it can be assumed that $\Delta V_2 - \Delta V_1 = \text{constant}$. Then,

$$\frac{\Delta V_2 - \Delta V_1}{m} = \frac{1}{m} \int_0^1 (V_2 - V_1) d\varphi \quad (9)$$

In order to eliminate uncertainty related to the fact that the detection is actually limited to the concentration φ_{\min} , it is expedient to have one experimental point measured by the static adsorption technique at the lowest detectable concentration. Finally, we can write

$$f(\varphi) = \frac{1}{m} \int_0^{\varphi} (V_2 - V_1) d\varphi = f(\varphi_{\min}) + \frac{1}{m} \int_{\varphi_{\min}}^{\varphi} (V_2 - V_1) d\varphi - \frac{1}{m} \int_{\varphi_{\min}}^1 (V_2 - V_1) d\varphi \quad (10)$$

Figs. 4 and 5 compare adsorption data obtained by the static and the dynamic techniques. The peculiar case is the determination of adsorption isotherms in the case of

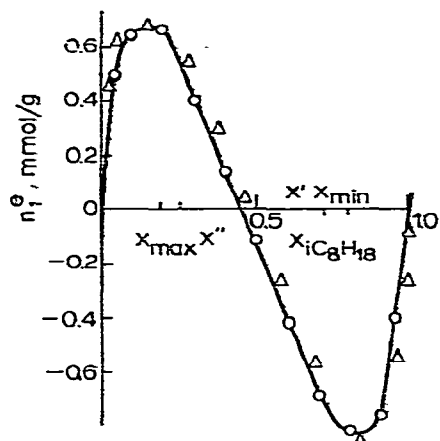


Fig. 6. Surface excess isotherm for the system isooctane-ethanol on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

S-shaped adsorption isotherms (Fig. 6). In this instance concentration points of $\varphi < \varphi_{max}$ and $\varphi > \varphi_{min}$ are moving at speeds greater than those of maximum and minimum points. Therefore, for example, for the system isooctane-ethanol, upon elution all concentration points at $\varphi > \varphi_{max}$ are washed out as a sharp self-narrowing front and only the points on the isotherm up to $\varphi = \varphi'$ can be calculated from the elution curve. Therefore, in the calculation the whole adsorption isotherm, the curve of the elution of ethanol from isooctane should be taken into account. In this instance concentration points at $\varphi > \varphi_{min}$ are eluted in the form of a broadened front, whereas all points at $\varphi < \varphi_{min}$ appear as a self-narrowing front. From such a curve the adsorption isotherm can be found only for the concentration points at $1 > \varphi > \varphi''$.

Figs. 7-10 compare the data obtained from the static (triangles) and the dynamic (circles) adsorption experiments. There is fairly good agreement between the results.

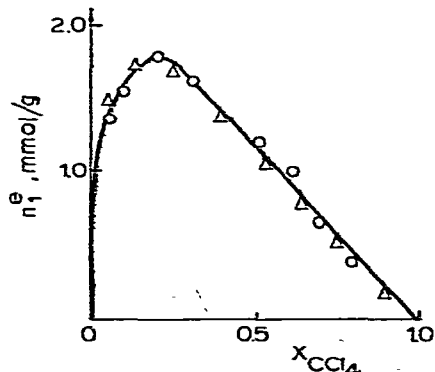


Fig. 7. Surface excess isotherm for the system carbon tetrachloride-ethanol on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

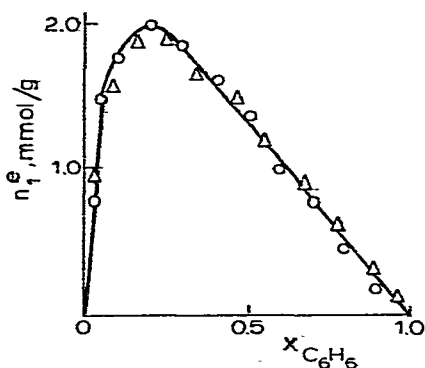


Fig. 8. Surface excess isotherm for the system benzene-ethanol on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

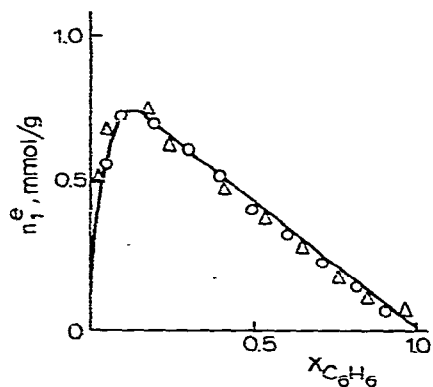


Fig. 9. Surface excess isotherm for the system benzene-carbon tetrachloride on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

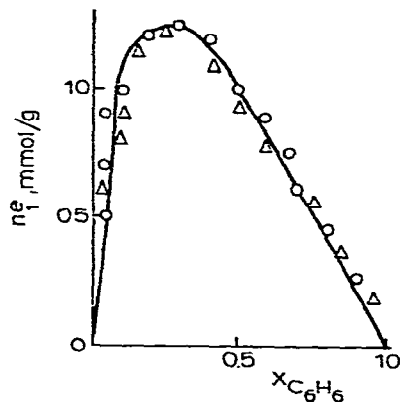


Fig. 10. Excess adsorption isotherm for the system benzene-isooctane on charcoal. O, Chromatographic method of measurement; Δ , static method of measurement.

CONCLUSION

The proposed method allows one to make measurements in the absence of extraneous gases with high accuracy over a wide range of temperatures and pressures. Also, unlike the static technique, the measurements can be easily automated. Studies of adsorption isotherms for benzene-isooctane, benzene-carbon tetrachloride, ethanol-benzene and ethanol-isooctane solutions on the same adsorbents gave similar results.

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