Adsorption 11: 67–72, 2005

Chromatographic Detectors in Systems of Three Components

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Abstract. The chromatographic theory for the adsorption in binary systems has been well-established over the years. A binary mixture of known composition flows through a column packed with adsorbent. The system is then disturbed by adding a pulse of one of the pure components, and this causes a composition front to travel through the column. The retention time of this composition front is measured with a detector. This retention time can be related to the isotherm gradients of the two components. The situation is more complicated for a system of three components. In this case there are two composition fronts, and it is not easy to relate the retention times to the three isotherm gradients. In this preliminary investigation, we present a new theory to show how by using *another* composition detector, it is possible to evaluate the composition retention time for each component. We present some data for the ethane-ethylene-helium-13X zeolite system, and show that a simple detector based on the measurement of viscosity might be suitable.

Keywords: adsorption, chromatography, retention time, binary mixtures

Background

Accurate and consistent adsorption measurements are required in the design of adsorption processes, the testing of new materials and for checking predictive methods. However, there is a dearth of binary and especially ternary adsorption data in the literature (Talu, 1998; Siperstein and Myers, 2001). The conventional approach to measure adsorption isotherms is to use a static (gravimetric or volumetric) method. Here, a gas mixture of known composition is allowed to equilibrate with a known amount of adsorbent. After equilibrium is reached, the total amount adsorbed is *either* determined using a sensitive balance or by pressure/volume measurements.

We however prefer an approach based on the chromatographic philosophy for a number of reasons. First, the equipment is robust and relatively cheap. Second, the measurements are relatively quick. Third, over the years at Loughborough we have developed our own sensitive molar flow meter capable of measuring flow rate changes of the order of (nL/s). This extra measurement allows us to observe the approach to equilibrium, complete a material balance on the adsorption column, and has led to a number of related applications. Fourth, because the chromatographic technique is differential, we have *internal* consistency tests not available in other methods.

We have applied our method to measure binary isotherms at constant pressure (Mason et al., 1997) and at variable pressure to measure the partial differential gradients (Heslop et al., 1998) and the natural progression is to investigate ternary isotherms at constant pressure. However, the subject of ternary isotherms has almost become a taboo subject. Tondeur et al. (1996) approached the problem for systems in

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which a non-adsorbed component is present in the mixture.

Perturbation Flows and Pulses

At this stage it is helpful to consider how the disturbance is made in chromatographic methods. The standard way is to add a pulse of gas. However, we prefer to add a perturbation flow. There are important distinctions between the two approaches. For the pulse method, the system returns to the original state (after the pulse has left the column). However, the addition of the perturbation flow necessarily gives a *different* steady-state. Consider that a perturbation of molar flow rate m and mole fraction y_{AP} is added to a main flow of molar flow rate M and mole fraction $y_{\mathrm{A}}(0)$. The total gas concentration in the column remains unchanged at c_{T}. From a material balance, the gas concentration of component A in the adsorption column changes by:

$$\begin{aligned}\Delta y_{\mathrm{A}} &= \frac{m}{M+m}(y_{\mathrm{AP}} - y_{\mathrm{A}}(0)) \\ &\rightarrow \Delta c_{\mathrm{A}} = c_{\mathrm{T}}\frac{m}{M+m}(y_{\mathrm{AP}} - y_{\mathrm{A}}(0)) \quad (1)\end{aligned}$$

Note the requirement that c_{T} remains constant during the perturbation. This might be hard to achieve because the increase in flow caused by adding the perturbation will lead to *some* increase in the system pressure. This can be shown to be negligible assuming that the column pressure drop is not excessive.

Chromatographic Method for Binary Systems

Figure 1 shows a basic arrangement used to determine binary adsorption isotherms. The mixture of interest (this can be pure A, pure B or a binary mixture of A and B) is produced by blender 1 and flows through the column packed with the required adsorbent. The perturbation gas (usually pure A or pure B) is produced by blender 2. An experiment is conducted by switching the 3-port valve which adds the perturbation flow to the main flow entering the adsorption column. The retention time is the time taken for the composition front to travel through the column and is measured with the thermal conductivity detector (TCD). We consider the material balance on the column, and so the composition retention time for each component (τ_{A} and τ_{B}) is defined by Mason and Buffham (1996):

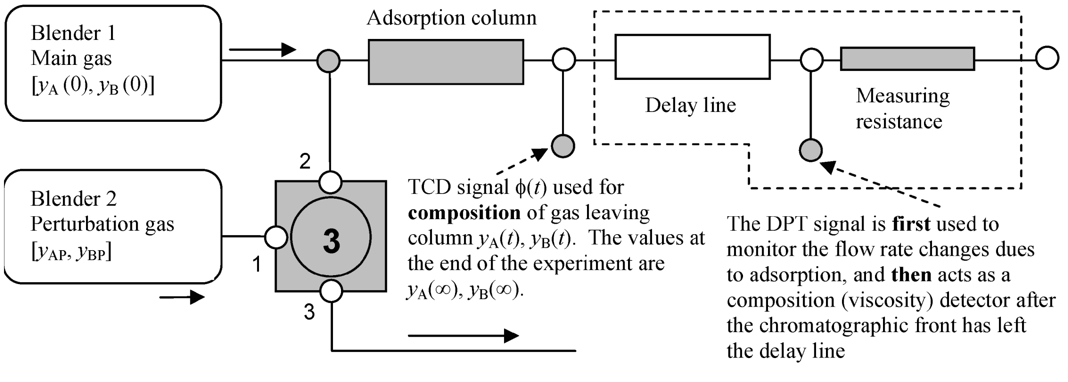
$$\tau_{\mathrm{A}} = \int_0^\infty \frac{y_{\mathrm{A}}(\infty) - y_{\mathrm{A}}(t)}{y_{\mathrm{A}}(\infty) - y_{\mathrm{A}}(0)}dt \quad (2)$$

$$\tau_{\mathrm{B}} = \int_0^\infty \frac{y_{\mathrm{B}}(\infty) - y_{\mathrm{B}}(t)}{y_{\mathrm{B}}(\infty) - y_{\mathrm{B}}(0)}dt \quad (3)$$

However, for the *unique* case of a binary system, the mole fractions necessarily sum to unity and we can write:

$$\begin{aligned}y_{\mathrm{A}}(0) + y_{\mathrm{B}}(0) = 1 &\rightarrow y_{\mathrm{A}}(\infty) + y_{\mathrm{B}}(\infty) \\ &= 1 \rightarrow y_{\mathrm{A}}(t) + y_{\mathrm{B}}(t) = 1 \quad (4)\end{aligned}$$

Consider how to determine τ_{A} and τ_{B}. The standard detector is based on the measurement of thermal conductivity (TCD). We assign the symbol ϕ for the TCD signal. For a binary system *only*, the following



TCD signal $\phi(t)$ used for **composition** of gas leaving column $y_A(t), y_B(t)$. The values at the end of the experiment are $y_A(\infty), y_B(\infty)$.

The DPT signal is **first** used to monitor the flow rate changes dues to adsorption, and **then** acts as a composition (viscosity) detector after the chromatographic front has left the delay line

Figure 1. Schematic experimental arrangement to determine binary adsorption isotherms.

simplification applies:

$$\tau_A = \tau_B = \int_0^\infty \frac{\phi(\infty) - \phi(t)}{\phi(\infty) - \phi(0)} dt \qquad (5)$$

The two retention times are *equal* and are obtained from the detector signal. For binary systems, there is a *single* composition front and τ_A (or τ_B) is the time taken for the front to travel through the column. This time is then used in the material balance to complete the material balance and determine the isotherm gradient for each component.

Extension of Method to Ternary Systems

Ternary systems are problematic because a perturbation to the system gives *two* composition fronts and we cannot use Eqs. (3) and (4). The problem is how to use the detector signal to deal with systems of three components. For the column material balance, there is now an extra retention time for the third component (C), defined by:

$$\tau_C = \int_0^\infty \frac{y_C(\infty) - y_C(t)}{y_C(\infty) - y_C(0)} dt \qquad (6)$$

For a system of three components, the restriction on the mole fractions now gives:

$$\begin{aligned} &y_A(0) + y_B(0) + y_C(0) \\ &\quad = 1 \rightarrow y_A(\infty) + y_B(\infty) + y_C(\infty) \\ &\quad = 1 \rightarrow y_A(t) + y_B(t) + y_C(t) = 1 \end{aligned} \qquad (7)$$

The question is how now to unravel the values of τ_A, τ_B and τ_C from the response of the TCD. We can represent the response of the TCD by Eq. (9) where ϕ_A and ϕ_B are the partial derivatives:

$$\phi(t) - \phi(0) = \phi_A[y_A(t) - y_A(0)] + \phi_B[y_B(t) - y_B(0)] \qquad (8)$$

Now consider the *overall change* in the detector signal caused by adding the perturbation gas (P).

$$\begin{aligned} \phi(\infty) - \phi(0) = {} & \phi_A[y_A(\infty) - y_A(0)] \\ & + \phi_B[y_B(\infty) - y_B(0)] \end{aligned} \qquad (9)$$

Finally, we now consider a second detector measuring a *different* physical property. For the time being, the symbol θ will be used to represent the signal of the second detector. There will be analogous Eqs. to (8) and (9) for the second detector. These four equations can be combined to give the following expression:

$$\tau_A = \int_0^\infty \frac{[\phi(\infty) - \phi(t)] - (\phi_B/\theta_B)[\theta(\infty) - \theta(t)]}{[\phi(\infty) - \phi(0)] - (\phi_B/\theta_B)[\theta(\infty) - \theta(0)]} dt \qquad (10)$$

$$\tau_B = \int_0^\infty \frac{[\phi(\infty) - \phi(t)] - (\phi_A/\theta_A)[\theta(\infty) - \theta(t)]}{[\phi(\infty) - \phi(0)] - (\phi_A/\theta_A)[\theta(\infty) - \theta(0)]} dt \qquad (11)$$

It is interesting at this stage to compare Eqs. (10) and (5): if the *magnitude* of the ratio (ϕ_B/θ_B) is *very small*, then the value of τ_A is mainly determined by the TCD record. As this ratio tends to zero, the TCD (ϕ) depends *only* on the presence of component A and the detector is classified as *A-specific*. This is regarded as the favoured situation in multi-component chromatography. In general, however, each detector signal depends on the presence of both components. For a ternary system, the value of τ_A can *possibly* be obtained from the responses of two detectors. The problem might arise if the denominator in Eq. (10) tends to zero. This reduces to:

$$\begin{aligned} &[\phi(\infty) - \phi(0)] - (\phi_B/\theta_B)[\theta(\infty) - \theta(0)] \\ &\quad = 0 \rightarrow \frac{\phi_A}{\phi_B} = \frac{\theta_A}{\theta_B} \end{aligned} \qquad (12)$$

This confirms what would be expected from intuition. If the two detectors respond in the *same* or *similar* ways to both components, then both detectors give essentially the same information and the combination of the two cannot be used to unravel the individual values of τ_A and τ_B. In summary, by combining the signals of two composition detectors, it is possible to back out the three composition retention times (τ_A, τ_B and τ_C).

Relationship between the Three Composition Retention Times

Equation (1) is useful because it shows how the overall change in mole fraction of component A caused by the perturbation flow depends on the mole fraction of component A in the carrier flow. There are also equivalent equations for components B and C. By combining

Eqs. (1) to (3), (6) and (7), we obtain:

$$\tau_A(y_{AP} - y_A(0)) + \tau_B(y_{BP} - y_B(0)) + \tau_C(y_{CP} - y_C(0)) = 0 \tag{13}$$

This is important because it shows that the relationship between the three retention times depends on the composition of the perturbation gas. Note the symmetry of Eq. (15). Note also that for a *binary* system of components A and B, the values of y_{CP} and $y_C(0)$ become zero and Eq. (15) reduces to Eq. (5).

Experimental Data

In order to explain some of the new concepts, it is helpful to consider what a typical experiment for a ternary system might look like. The experiment is adding an ethane perturbation to a main flow of helium (80%) and ethylene (20%). The flow rate of the perturbation flow is around 1% that of the main (carrier) flow.

Discussion

Let us first consider the DPT record in Fig. 2. The presence of the delay-line ensures that the composition of the gas in the measuring resistance is constant during the time frame shown in Fig. 2. This means that the DPT signal is *solely* determined by the molar flow-rate of the gas flow leaving the column. The integrated response can therefore be used to determine the overall change of inventory (number of moles) during the experiment. The perturbation flow of approximately 2 mL/min causes the baseline to move from 25.7 to 118.3 mV. Without the adsorption column, the signal would move *directly* from 25.7 to 118.3 mV. This shows the incredible power of using a DPT, flow resistances and delay lines to monitor tiny changes in flow rate.

Figure 3 shows what would be observed using a typical chromatographic detector (TCD). For a binary system, the TCD signal would simply sweep from the initial value to the final value. The overshoot is caused by the presence of the extra composition front. The TCD works by monitoring the thermal conductivity of the gas flow leaving the column. We know the composition corresponding to the initial baseline $\phi(0)$; this is 80% helium and 20% ethylene. We need to calculate the composition corresponding to the final baseline $\phi(\infty)$. Using Eq. (1) for each component, we can calculate the overall change in mole fraction for each component. The ethane perturbation flow rate (m) is roughly 1% of the main flow rate (M). This gives the ethane composition of the final mixture is close to 1%, with the helium and ethylene compositions changing to 79.2 and 19.8% respectively. Importantly, the compositions at all intermediate points are *unknown* and this shows why a single composition detector is insufficient for ternary systems.

Figure 4 shows the DPT record some time later. The molar flow rate of the gas leaving the column in Fig. 4 is constant because the composition front had

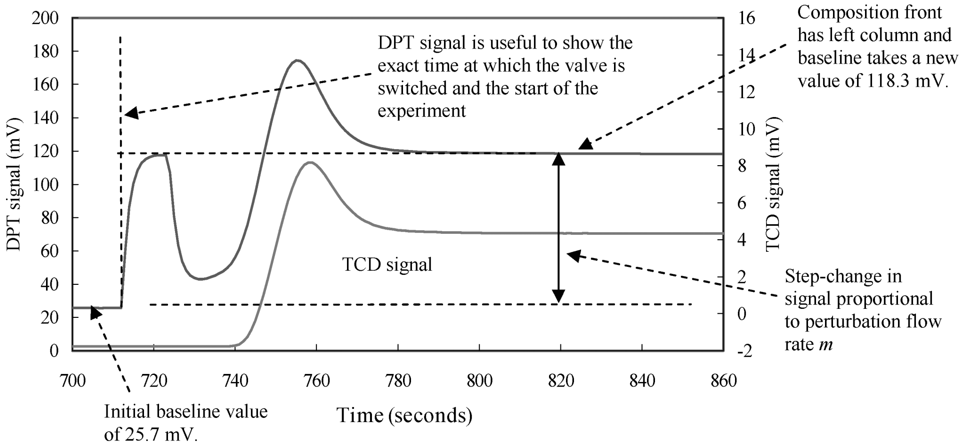


Figure 2. DPT (flowrate) and TCD (composition) records for a ternary adsorption experiment. The experiment is conducted by adding the perturbation at a time of 712 seconds.

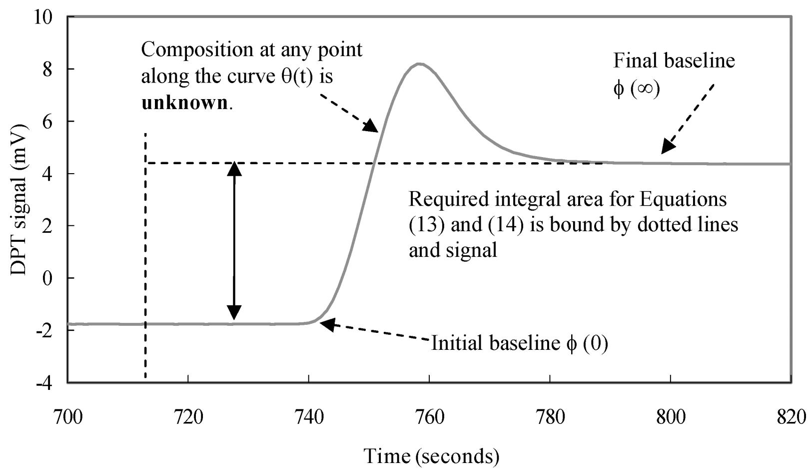


Figure 3. The TCD (composition) record from Fig. 2 shown in more detail. The change in baseline from $\phi(0)$ to $\phi(\infty)$ is caused by the ethane perturbation flow. For a binary experiment, there is a simple sweep between the baselines. The peak toward some intermediate composition is characteristic of a ternary adsorption experiment.

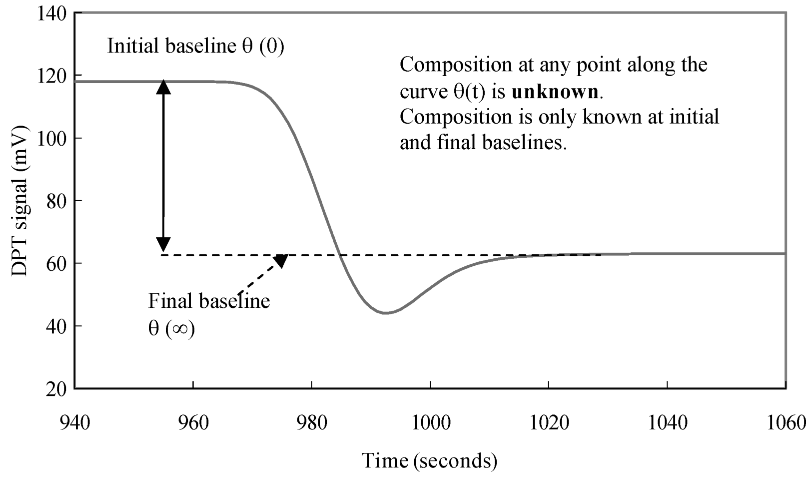


Figure 4. The DPT (viscosity) record for the same experiment some time later, as the composition front leaves the delay line. Note that the scale is different from that in Fig. 2. The flow rate is constant and the DPT variation is caused by the variation in viscosity with composition. The change in baseline from $\theta(0)$ to $\theta(\infty)$ is caused by the ethane perturbation flow.

left the column by a time of around 800 seconds (see Fig. 2). Now, the DPT signal is solely determined by the viscosity of the gas mixture leaving the column. The fact that the shapes of the composition records in Figs. 3 and 4 are similar in shape might suggest that the thermal conductivity and viscosity of the 80% mixture vary in similar ways when the same perturbation is applied. The overall length of the composition front is similar in both Figs. 3 and 4, perhaps implying that the presence of the delay-line does not have a significant dispersive effect on the DPT (viscosity) record.

Conclusions

For a binary system, only one detector is required to determine the composition retention time for each component (τ_A and τ_B). These composition retention times have the same value. The main requirement is that the signal of the detector varies with the composition of the binary gas mixture. For ternary systems, however, there is an extra composition retention time for the third component (τ_C). From a simple consideration of mole fractions and the fact that they sum to unity, we can show that the three retention times for a particular experiment (τ_A, τ_B and τ_C) are *not* the same and depend on the composition of the perturbation flow. These three retention times can only be obtained by using another composition detector. The response of a detector for a ternary system can be characterised by the ratio of the partial derivatives (ϕ_A/ϕ_B or θ_A/θ_B). The three retention times (τ_A, τ_B and τ_C) can be calculated by combining the areas and offsets from the two detectors. This method is based entirely on a simple material balance and does not require any assumptions to be made regarding rate processes.

Acknowledgment

One author (MJH) greatly acknowledges the financial support of the *Royal Society* in the form of a Conference Grant (2004/R1) and the *Royal Academy of Engineering* in the form of an International Travel Grant.

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