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Binary chromatographic retention times from perturbations in flowrate and composition

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Abstract This work is a theoretical and experimental investigation of the binary retention time (t_{step}) when the disturbance is made to a chromatographic system by adding a small flow of one of the pure components. The established theory is for addition of a pulse: in this case, the retention time (t_{pulse}) depends on the two binary isotherm gradients, and should be independent of the choice of pulse gas. From the column material balance, the value of t_{step} also depends on the column pressure drop and perturbation gas—the value of t_{step} should always be greater for the more-adsorbed component. The theory has been validated from results on the nitrogen–argon–5A zeolite system at 25, 54 and 81 °C. For a 50% mixture at 25 °C with a column pressure drop of 0.1 bar, the values of t_{step} are 257 and 254 seconds for the nitrogen and argon perturbations. The values of t_{step} are different because addition of the perturbation flow causes a very small *increase* in average column pressure (about 0.5 mbar), which causes the binary isotherm gradients to be measured in (slightly) different directions along the isotherm surface. The intention is to determine the value of t_{step} for the case of a *zero change* in the average column pressure: experimentally, this would require a column with a zero pressure drop. The material balance shows that t_{step} for a column with a zero pressure drop is obtained from a simple weighted function of the values of t_{step} for the two pure-component perturbations. Accurate determination is essential because the "zero pressure drop" values are used to determine binary adsorption isotherms which are, of course, at a fixed pressure.

Keywords Binary adsorption · Retention time · 5A zeolite · Column pressure drop

Abbreviations

a_1	Henry's constant for component A [m^3 kg^{-1}]
a_2	Langmuir constant for component A [m^3 mol^{-1}]
b_1	Henry's constant for component B [m^3 kg^{-1}]
b_2	Langmuir constant for component B [m^3 mol^{-1}]
c_A	Gas-phase concentration of component A in column [mol m^{-3}]
c_B	Gas-phase concentration of component B in column [mol m^{-3}]
c_T	Total gas-phase concentration of components A and B in column [mol m^{-3}]
F_A	Correction factor to allow for the change of c_A in the column
F_B	Correction factor to allow for the change of c_B in the column
G	Correction factor to allow for the change of c_A in the column [m^3 kg^{-1}]
K_A	Measured binary equilibrium constant for perturbation A [mL g^{-1}]
K_B	Measured binary equilibrium constant for perturbation B [mL g^{-1}]
K_{CP}	Binary equilibrium constant for constant column pressure [mL g^{-1}]
K_{step}	Measured binary equilibrium constant for general perturbation [mL g^{-1}]

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K_{mix}	Measured binary equilibrium constant for mixture perturbation [mL g^{-1}]
P	Dimensionless column pressure drop
P_{cmean}	Mean column pressure [bar]
P_{cout}	Outlet column pressure [bar]
Q	Mean volumetric flowrate in column [mL s^{-1}]
R_{AB}	Ratio of the Henry's constants for components A and B
t_{A}	Measured retention time for perturbation A [s]
t_{B}	Measured retention time for perturbation B [s]
t_{CP}	Retention time for column with negligible pressure drop [s]
t_{g}	Measured retention time for unretained pulse [s]
t_{pulse}	Measured retention time for pulse of one of components [s]
t_{step}	Measured retention time for small and fixed perturbation flow [s]
V_{g}	Volume of gas space in system between valve and detector [mL]
W	Mass of adsorbent in column [g]
w_{A}	Amount of component A adsorbed in mixture [mol kg^{-1}]
w_{A}^0	Pure-component amount adsorbed of component A [mol kg^{-1}]
w_{B}	Amount of component B adsorbed in mixture [mol kg^{-1}]
w_{B}^0	Pure-component amount adsorbed of component B [mol kg^{-1}]
y_{A}^0	Mole fraction of component A in main (or carrier) gas
$y_{\mathrm{A}}^{\mathrm{p}}$	Mole fraction of component A in perturbation gas
y_{B}^0	Mole fraction of component B in main (or carrier) gas
$y_{\mathrm{B}}^{\mathrm{p}}$	Mole fraction of component B in perturbation flow
ΔP_{c}	Pressure drop across column [bar]
ΔP_{r}	Pressure drop across flow resistance [bar]
$\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^0)\right]$	Normalised gradient of viscosity with composition at mole fraction y_{A}^0

1 Background

Consider a binary-gas mixture of components A and B at equilibrium with a solid adsorbent. At a particular temperature, the equilibrium relations between the amounts adsorbed of each component per unit mass of adsorbent (w_{A} and w_{B}) and the molar concentrations in the gas phase (c_{A} and c_{B}) are the *adsorption isotherms*:

$$w_{\mathrm{A}} = w_{\mathrm{A}}(c_{\mathrm{A}}, c_{\mathrm{B}}) \tag{1}$$

$$w_{\mathrm{B}} = w_{\mathrm{B}}(c_{\mathrm{A}}, c_{\mathrm{B}}) \tag{2}$$

There are a number of experimental techniques for determining binary adsorption isotherms, and a recent review has been produced by Sircar (2007). In this work, the emphasis is on *chromatographic* techniques. The various chromatographic techniques have a number of factors in common. First, a carrier (or main) gas with concentrations c_{A} and c_{B} flows at a steady rate through a column packed with a small amount of adsorbent. Second, a change is made to the carrier gas before the column; this is usually by the addition of a small pulse of one of the pure components. Third, the composition of the gas stream leaving the column is monitored with a detector such as a thermal conductivity detector (TCD): the variation of the composition with time can be used to carry out a material balance on the column, and by implication the amount of each component adsorbed in the column. The whole procedure is repeated for various carrier compositions, ranging from pure A ($c_{\mathrm{B}} = 0$) to pure B ($c_{\mathrm{A}} = 0$) and the results tabulated to determine the binary adsorption isotherms. There are a number of advantages of chromatographic techniques over static techniques: low capital costs; applicability to both small and large adsorbent amounts; fast experimental times; and the self-checking consistency that derives from making changes to a system at equilibrium.

The various chromatographic techniques differ in the way the change or perturbation is made to the system. The group of Harlick and Tezel at Ottawa achieve this by adding small pulses (typically 1 mL) of each of the pure components, and Fig. 1 shows a generic experimental arrangement. Initially, a main flow with mole fraction (y_{A}^0) of component A flows through the column at volumetric flowrate Q. The perturbation gas with mole fraction ($y_{\mathrm{A}}^{\mathrm{P}}$) flows through the 6-port valve. An experiment is initiated by switching the valve, which allows a volume of the carrier gas to be replaced with an equal volume of the perturbation gas, without the problems of a large flow surge. The total gas concentration (c_{T}) in the column is determined from the average column pressure. The retention time (t_{pulse}) is the time taken for the transient to pass through the column and arrive at the detector. Peterson and Helfferich (1965) derived an expression for the binary isotherm gradients at the main-gas composition (y_{A}^0). They assumed that the concentration changes caused by adding the pulse were small, and that the mean column pressure would remain constant during the experiment. This is conveniently represented using the binary equilibrium constant (K) as follows

$$K_{\mathrm{CP}} = (t_{\mathrm{pulse}} - t_{\mathrm{g}})\frac{Q}{W} = y_{\mathrm{B}}^0 \frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{A}}} + y_{\mathrm{A}}^0 \frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{B}}} \tag{3}$$

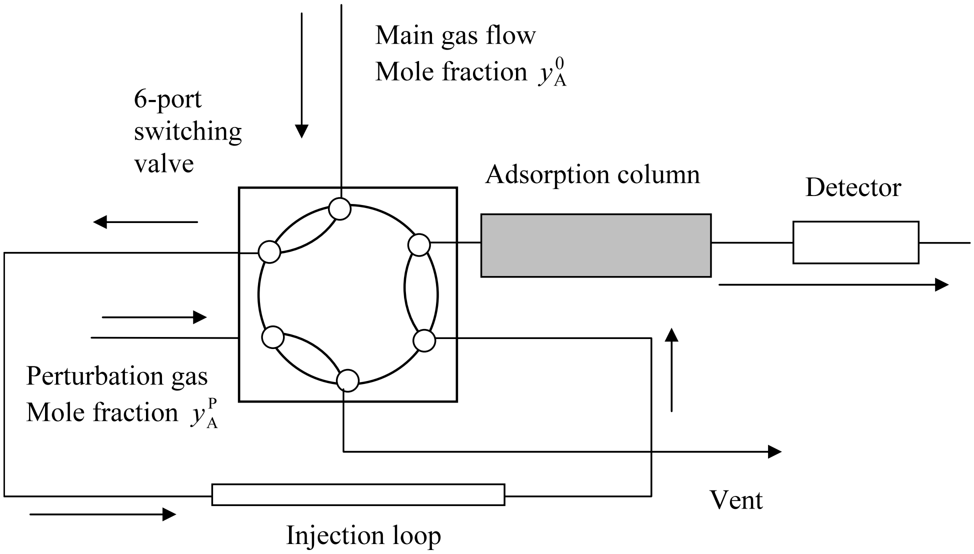

Fig. 1 Schematic experimental arrangement for the determination of chromatographic retention times from the addition of *pulses*

where W is the mass of adsorbent and the non-retained pulse time (t_g) can be obtained directly from injecting a pulse of non-adsorbed substance into the column, or indirectly from

$$t_g = \frac{V_g}{Q} \tag{4}$$

where V_g is the total volume of gas space in the system (between the valve and detector) which includes the space *between* the pellets, the space *inside* the pellets and any other empty volume. The advantage of injecting a pulse of non-adsorbed substance is that it avoids knowledge of the value of V_g—which can be significant—because these contributions cancel out in the ($t_{\text{pulse}} - t_g$) term (Hyun and Danner 1982). Estimating the value of t_g is not so critical in systems of highly-adsorbed gases ($t_{\text{pulse}} \gg t_g$); as we shall see later, this is not the case for the nitrogen–argon–5A zeolite system. The term on the right-hand-side of (3) is the binary equilibrium constant—also termed K_{CP}—the subscript indicating constant column pressure or constant gas concentration (c_T). The significance of this subscript (CP) will become apparent in the next section. The form of the equation suggests that the value of t_{pulse} should be *independent* of the choice of perturbation gas.

There are, however, still potential problems associated with adding discrete pulses. For example, it is likely that at the entrance to the column, the pulse will have a central region of essentially pure (perturbation) gas. The composition of the pulse will vary, at least initially, significantly across its length, and this almost certainly violates the assumption that any changes in composition should be small. Tezel et al. (1999) measured pulse retention times for the nitrogen–krypton system using two different zeolites. They found a systematic difference between the retention times obtained using nitrogen and krypton pulses. Note also that (3) includes two "unknown" isotherm gradients for one retention time. Harlick and Tezel (2001, 2003) circumvented this problem by assuming a functional form for the adsorption isotherms, and term this the HT–CPM method.

Brandani and Ruthven (2003) have developed a method to deal with binary adsorption using a modification of the zero length column (ZLC) technique. This involves first contacting the adsorbent with a carrier gas consisting of helium with the two adsorbable components (A and B). Then, at time zero, the column is purged with pure helium, but at the same volumetric flow rate. The mole fractions of both components are then monitored in the outlet flow from the column. Assuming that the purge flow is low enough, the outlet stream can be considered to be at equilibrium with the adsorbed phase: the variations of the two mole fractions can then be used to complete the material balance and determine the amounts adsorbed of each component. The group of Buffham and Mason at Lougborough have adopted an approach that is different in two ways from other methods: a step change is made to the composition of the carrier flow (rather than a discrete pulse) and the variation in the outlet flow from the column is also monitored. One alternative to adding pulses is to make a step change in composition—but *not* flowrate—of the gas flowing through the column. Figure 2 shows a possible experimental arrangement. As shown, the first main flow of mole fraction y_A^0 is flowing though the column. The second main gas should have exactly the same flow rate of the first main gas, but the mole fraction should differ by say 0.01. The advantage of the step-change method is that the composition of the gas across the transient is well defined and will vary between the compositions of the two main flows. One practical problem is that it is exceedingly difficult to have the two main flow rates matched exactly.

The advancement is to make a step change in *both* flowrate and composition. This is achieved by adding a small

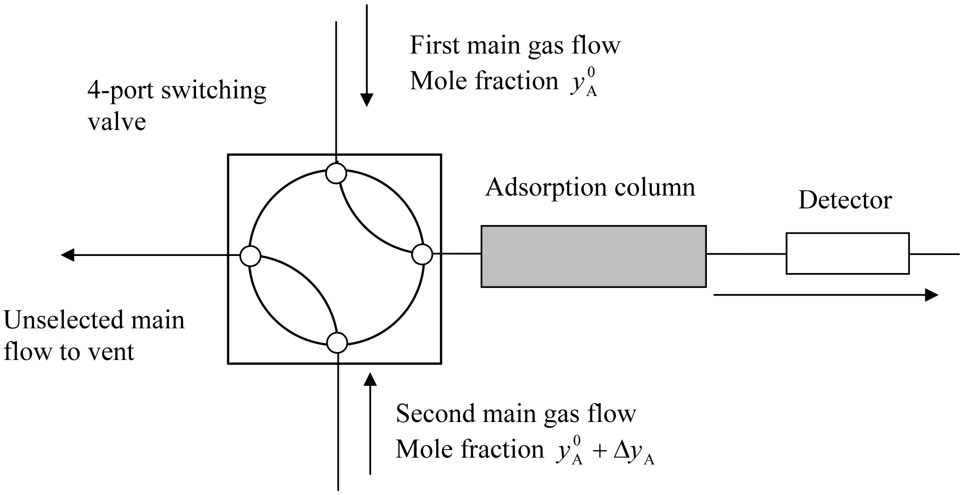

Fig. 2 Schematic experimental arrangement for the determination of chromatographic retention times from *step-changes in composition only*

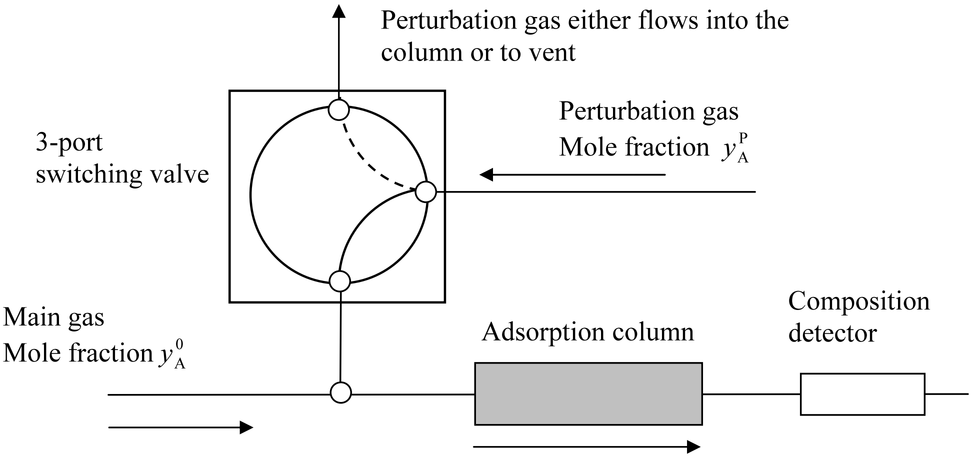

Fig. 3 Schematic experimental arrangement for the determination of chromatographic retention times from *step-changes in composition and flow rate*

flowrate (termed perturbation) of one of the pure components. Figure 3 shows a typical experimental arrangement including a 3-port valve. The extra component of equipment is a mass flow controller (MFC) and this is required to deliver a steady flow rate of the order of 0.1 mL/min. From the variation of the TCD (composition) record, the composition retention time (t_{step}) is determined: this is basically the time taken for the composition front to travel through the column. The motivation for this work is that there is a systematic difference between the values of t_{step} for each perturbation gas. For the nitrogen–argon–5A zeolite system, the retention time obtained for the nitrogen perturbation gas is usually greater than that for the argon perturbation. The discrepancy varies from one to five seconds in measured values ranging from 200 to 400 seconds (Heslop 1993). Moreover, with an increase in column pressure drop, the discrepancy increased to more than 10 seconds (Heslop et al. 1998). This is significant, being greater than the experimental error. Since the perturbation flow is small (typically 1% of the main flow), the difference cannot be caused by violation of the "composition changes" constraint. The basic assumption is that the mean gas concentration in the column (c_T) should remain constant during the experiment. However, from previous work (Mason and Buffham 1996b), adding a perturbation flow *increases* the mean column pressure P_{cmean} and hence the value of c_T.

Based on the literature review and our findings, there are three objectives to this work:

1. To derive an analytical expression for the composition retention time (t_{step}) for perturbation flows, which should include the pressure drop down the column (ΔP_c) and the composition of the perturbation flow. The intention is to obtain the value of retention time which *would be* obtained for a column with zero pressure drop. Addition of the perturbation might typically increase P_{cmean} by only 0.1 mbar, but even this can affect the value of t_{step}.
2. To validate this expression by comparing with available data for the nitrogen–argon–5A zeolite system. For example, can the analytical expression confirm that the nitrogen retention time is always greater than the argon time, and that the difference in the values of t_{step} for a

column pressure drop of 0.1 bar should be a couple of seconds?

3. The third objective concerns how the t_{step} values are processed to determine the binary isotherms. To this effect, an optimisation routine based on the binary-Langmuir theory, proposed by Buffham et al. (1999) is considered. A set of t_{step} values can be processed using the routine to give the three parameters of the binary-Langmuir isotherm: the two pure-component amounts adsorbed and the ratio of the Henry constants. Since the set of t_{step} values using the nitrogen perturbation is (slightly) different to that using the argon perturbation, a different set of fitting parameters would be expected for each set of data. It is interesting to compare the parameters for each set of data: for example, if the retention times vary by about 1%, would we expect the fitting parameters also to vary by 1%?

The first objective (development of material balances) is covered in Theory 1 and Theory 2. To improve clarity, it is found helpful to divide the complete theory for this work into three stages. The second objective (comparison of measured retention times) is covered in Theory 1 and the Experimental data section. The third objective (processing of retention times to predict binary adsorption isotherms) is covered in Theory 3 and Sect. 6.

2 Theory 1: derivation of general expression for composition retention time (t_{step})

In this section, the derivation of a general expression for the composition retention time and the corresponding binary equilibrium constant (K_{step}) will be shown. A good starting point is a concise review of the work carried out by the group of Buffham and Mason at Loughborough on the development of perturbation chromatography to include monitoring of the outlet flow rate from the column. This development is shown in Mason and Buffham (1996a, 1996b) and Mason et al. (1997). To summarise, an experiment is carried out by adding a small perturbation flow to a larger carrier (or main) flow. The variation of the detector from the composition detector is used to determine the (standard) composition retention time (t_{step})—as described before. The variation in the column outlet flow rate is used to determine the flowrate retention time (t_n) are obtained from the composition and flow rate detector records respectively. As a matter of interest, the value of t_n can be positive or negative, depending upon whether addition of the perturbation causes net adsorption or net desorption. In this work, however, the emphasis is solely on the composition time. The material balance can be written for each component as

$$W\frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{A}}}+V_{\mathrm{g}}=\frac{Q}{F_{\mathrm{A}}}\left[t_{\text{step}}+\frac{y_{\mathrm{A}}^{0}}{y_{\mathrm{A}}^{\mathrm{p}}-y_{\mathrm{A}}^{0}}t_{n}\right] \tag{5}$$

$$W\frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{B}}}+V_{\mathrm{g}}=\frac{Q}{F_{\mathrm{B}}}\left[t_{\text{step}}+\frac{y_{\mathrm{B}}^{0}}{y_{\mathrm{B}}^{\mathrm{p}}-y_{\mathrm{B}}^{0}}t_{n}\right] \tag{6}$$

where

$$\begin{aligned}F_{\mathrm{A}}=1+\frac{y_{\mathrm{A}}^{0}}{y_{\mathrm{A}}^{\mathrm{p}}-y_{\mathrm{A}}^{0}}\frac{\Delta P_{\mathrm{c}}}{2P_{\text{cmean}}}\frac{1+\Delta P_{\mathrm{c}}/3P_{\text{cout}}}{1+\Delta P_{\mathrm{c}}/3P_{\text{cout}}}\\ \times\left[1+(y_{\mathrm{A}}^{\mathrm{p}}-y_{\mathrm{A}}^{0})\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}\right](y_{\mathrm{A}}^{0})\right]\end{aligned} \tag{7}$$

and

$$\begin{aligned}F_{\mathrm{B}}=1+\frac{y_{\mathrm{B}}^{0}}{y_{\mathrm{B}}^{\mathrm{p}}-y_{\mathrm{B}}^{0}}\frac{\Delta P_{\mathrm{c}}}{2P_{\text{cmean}}}\frac{1+\Delta P_{\mathrm{c}}/3P_{\text{cout}}}{1+\Delta P_{\mathrm{c}}/3P_{\text{cout}}}\\ \times\left[1+(y_{\mathrm{A}}^{\mathrm{p}}-y_{\mathrm{A}}^{0})\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}\right](y_{\mathrm{A}}^{0})\right]\end{aligned} \tag{8}$$

Equations (7) and (8) define the column *correction factors* which allow for the fact that the mean column pressure (P_{cmean}) increases when the perturbation gas is added to the main flow. Note that (7) and (8) include a term in square brackets related to the (normalised) gradient of the viscosity of the mixture at the composition of the main flow. Note also that the situation can be simplified by using columns with a low pressure drop, since this causes both F_{A} and F_{B} to tend to unity and become independent of composition, allowing the material balance to be solved relatively easily. The flowrate retention time (t_n) can be eliminated from (5) and (6), giving

$$\begin{aligned}K_{\text{step}}&=(t_{\text{step}}-t_{\mathrm{g}})\frac{Q}{W}\rightarrow K_{\text{step}}\\ &=F_{\mathrm{A}}y_{\mathrm{B}}^{0}\frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{A}}}+F_{\mathrm{B}}y_{\mathrm{A}}^{0}\frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{B}}}\end{aligned} \tag{9}$$

It is important to point out that the gradients in (9) are *not* the same as those in (1) because those in (1) are at *constant pressure*: that is the total gas concentration (c_{T}) remains constant after the perturbation has been added whereas those in (9) reflect the fact that addition of the perturbation *increases* the value of c_{T} in the column. So, it is necessary to replace the full differentials in (9) with gradients based on the partial differentials. From the chain rule for partial differentials

$$\frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{A}}}=\left(\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{A}}}\right)_{c_{\mathrm{B}}}+\left(\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{B}}}\right)_{c_{\mathrm{A}}}\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{A}}} \tag{10}$$

$$\frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{B}}}=\left(\frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right)_{c_{\mathrm{A}}}+\left(\frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{A}}}\right)_{c_{\mathrm{B}}}\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{B}}} \tag{11}$$

Further substitution for F_{A} and F_{B} into (9) gives

$$K_{\text{step}}=y_{\mathrm{A}}^{0}\left[\frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{B}}}-\frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{A}}}\right]+y_{\mathrm{B}}^{0}\left[\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{A}}}-\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{B}}}\right]$$

$$+ PG\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^{0})\right] + PG\frac{1}{y_{\mathrm{A}}^{\mathrm{p}} - y_{\mathrm{A}}^{0}} \tag{12}$$

where

$$P = \frac{\Delta P_{\mathrm{c}}}{2P_{\mathrm{cmean}}}\frac{1 + \Delta P_{\mathrm{c}}/3P_{\mathrm{cout}}}{1 + \Delta P_{\mathrm{c}}/2P_{\mathrm{cout}}} \tag{13}$$

is a *dimensionless* pressure term that depends on the column pressure drop and the column outlet pressure. The terms P_{cout} and P_{cmean} are the outlet and mean column pressures respectively. The term G in (12) is defined by

$$G = y_{\mathrm{A}}^{0}y_{\mathrm{B}}^{0}\left(\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{A}}} - \frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right) + (y_{\mathrm{B}}^{0})^{2}\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{B}}} - (y_{\mathrm{A}}^{0})^{2}\frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{A}}} \tag{14}$$

and involves the four partial derivatives. Note that G is zero at both $y_{\mathrm{A}}^{0} = 0$ and $y_{\mathrm{A}}^{0} = 1$. Equation (12) can be simplified by considering the first two term on the left-hand side of the equation. For a *constant pressure* situation, the changes in gas-phase concentration are

$$c_{\mathrm{T}} = c_{\mathrm{A}} + c_{\mathrm{B}} \rightarrow \mathrm{d}c_{\mathrm{A}} + \mathrm{d}c_{\mathrm{B}} = 0 \rightarrow \frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{B}}} = -1$$

which means that the first two terms on the left-hand side are the isotherm gradients at constant pressure for components A and B respectively. Equation (12) can be simplified to

$$K_{\mathrm{step}} = K_{\mathrm{CP}} + PG\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^{0})\right] + PG\frac{1}{y_{\mathrm{A}}^{\mathrm{p}} - y_{\mathrm{A}}^{0}} \tag{15}$$

Equation (15) confirms that the retention time t_{step} will indeed vary with the composition of the perturbation gas. Furthermore, it confirms what we expect from intuition. As the value of ΔP_{c} tends to zero, the value of t_{step} approaches that for a column of zero pressure drop.

3 Theory 2: relation of K_{CP} to experiments involving pure and mixture perturbations

At this stage it is helpful to take stock and state the main purpose of this work. From a particular experiment the value of K_{step} is determined; however, the constant-pressure value (K_{CP}) is the *goal variable* because it involves the isotherm gradients at constant pressure—that is, constant total gas concentration (c_{T}). It is the value of K required in a procedure such as the polynomial fitting method to determine binary isotherms at constant pressure (van der Vlist and van der Meijden 1973). Consider now two separate experiments using a binary system with components A and B. In the first, perturbation gas A ($y_{\mathrm{A}}^{\mathrm{p}} = 1$) is used to determine the value of K_{A}. In the second, perturbation gas B ($y_{\mathrm{A}}^{\mathrm{p}} = 0$) is used to determine the value of K_{B}. Writing (15) for both perturbation gases:

$$K_{\mathrm{A}} = K_{\mathrm{CP}} + PG\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^{0})\right] + PG\frac{1}{1 - y_{\mathrm{A}}^{0}} \tag{16}$$

$$K_{\mathrm{B}} = K_{\mathrm{CP}} + PG\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^{0})\right] + PG\frac{1}{0 - y_{\mathrm{A}}^{0}} \tag{17}$$

These can be used to eliminate the PG term from each expression to give

$$K_{\mathrm{CP}} = y_{\mathrm{A}}^{0}K_{\mathrm{B}} + y_{\mathrm{B}}^{0}K_{\mathrm{A}} - \left[y_{\mathrm{A}}^{0}y_{\mathrm{B}}^{0}(K_{\mathrm{A}} - K_{\mathrm{B}})\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}\right](y_{\mathrm{A}}^{0})\right] \tag{18}$$

Interestingly, the value of K_{CP} can be obtained from a weighted expression of K_{A} and K_{B}, the results for each of the pure perturbation gases, and a correction factor involving the change in viscosity with composition. This last term is interesting because it involves viscosity only: in all previous cases, the viscosity term has included multiplication by a term involving the pressure drop of the column (ΔP_{C}).

It is instructive to take this process a stage further. Consider now a third experiment, using a *mixture* perturbation gas, which would require an extra blending machine. Let the perturbation have a *general* mole fraction of $y_{\mathrm{A}}^{\mathrm{p}}$ to give a K value of K_{mix}.

$$K_{\mathrm{mix}} = K_{\mathrm{CP}} + PG\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}\right](y_{\mathrm{A}}^{0}) + PG\frac{1}{y_{\mathrm{A}}^{\mathrm{p}} - y_{\mathrm{A}}^{0}} \tag{19}$$

Now consider the equations for K_{A} (16), K_{B} (17) and K_{mix} (19). These three equations can be used to eliminate K_{CP} and obtain a consistency test.

$$y_{\mathrm{A}}^{\mathrm{p}}y_{\mathrm{B}}^{0}(K_{\mathrm{A}} - K_{\mathrm{mix}}) = y_{\mathrm{B}}^{\mathrm{p}}y_{\mathrm{A}}^{0}(K_{\mathrm{B}} - K_{\mathrm{mix}}) \tag{20}$$

This symmetrical expression can be rearranged to a more convenient form:

$$K_{\mathrm{mix}} = \frac{K_{\mathrm{A}}}{1 - \frac{y_{\mathrm{B}}^{0}y_{\mathrm{A}}^{\mathrm{p}}}{y_{\mathrm{A}}^{0}y_{\mathrm{B}}^{\mathrm{p}}}} + \frac{K_{\mathrm{B}}}{1 - \frac{y_{\mathrm{A}}^{0}y_{\mathrm{B}}^{\mathrm{p}}}{y_{\mathrm{B}}^{0}y_{\mathrm{A}}^{\mathrm{p}}}} \tag{21}$$

For a main flow of pure B, (21) can be used to show that

$$(y_{\mathrm{A}}^{0} = 0,\ y_{\mathrm{B}}^{0} = 1) \rightarrow K_{\mathrm{A}} = K_{\mathrm{mix}}$$

and similarly for a main flow of pure A, substitution into (21) gives

$$(y_{\mathrm{B}}^{0} = 0,\ y_{\mathrm{A}}^{0} = 1) \rightarrow K_{\mathrm{B}} = K_{\mathrm{mix}}$$

This is important because the implication is that for pure-component main flows only, the retention time is *independent* of the composition of the perturbation gas. For example, for the main flow of pure A, the retention time for perturbation B should be the same as those for any of the mixture perturbations (for example, 25%, 50%, 75% and so on).

4 Theory 3: processing of values of t_{step} to determine binary isotherms

The measured data consists of sets of composition retention times with systematic differences: in general the retention time for the nitrogen perturbation is greater than that for argon. It is necessary to quantify the effects of these differences. For example, if the set of retention times for the nitrogen perturbation differ from the argon perturbation by 1% across the whole composition range, does this mean that the subsequent isotherm predictions will differ by 1%? One possibility is the polynomial-fitting method (van der Vlist and van der Meijden 1973) to determine the isotherm predictions for each perturbation gas. The problem is that this requires the input of the pure-component amounts adsorbed and we wish to restrict this study to retention time measurements *only*. Another approach is proposed by Buffham et al. (1999). This involves assuming that the isotherms are of the binary-Langmuir form, that is

$$w_{\mathrm{A}} = \frac{a_1 c_{\mathrm{A}}}{1 + a_2 c_{\mathrm{A}} + b_2 c_{\mathrm{B}}} \tag{22}$$

$$w_{\mathrm{B}} = \frac{b_1 c_{\mathrm{B}}}{1 + a_2 c_{\mathrm{A}} + b_2 c_{\mathrm{B}}} \tag{23}$$

where a_1 and b_1 are the Henry constants, and a_2 and b_2 are the Langmuir constants. For a *constant-pressure* system with a total gas concentration of c_{T}, the equilibrium constant is

$$K_{\mathrm{CP}} = y_{\mathrm{B}}^0 \frac{\mathrm{d}w_{\mathrm{A}}}{\mathrm{d}c_{\mathrm{A}}} + y_{\mathrm{A}}^0 \frac{\mathrm{d}w_{\mathrm{B}}}{\mathrm{d}c_{\mathrm{B}}}$$

$$\rightarrow K_{\mathrm{CP}} = \frac{y_{\mathrm{B}}(1 + b_2 c_{\mathrm{T}}) a_1}{(1 + a_2 c_{\mathrm{A}} + b_2 c_{\mathrm{B}})^2} \tag{24}$$

Note that the equation for K_{CP} has *four* parameters which can be simplified using:

$$w_{\mathrm{A}}^0 = \frac{a_1 c_{\mathrm{T}}}{1 + a_2 c_{\mathrm{T}}} \tag{25}$$

$$w_{\mathrm{B}}^0 = \frac{b_1 c_{\mathrm{T}}}{1 + b_2 c_{\mathrm{T}}} \tag{26}$$

where w_{A}^0 and w_{B}^0 are the pure-component amounts adsorbed. These substitutions can finally be used to give a *three-parameter* equation for the binary equilibrium constant

$$K_{\mathrm{CP}} = \frac{\frac{R_{\mathrm{AB}} y_{\mathrm{B}}}{w_{\mathrm{B}}^0 c_{\mathrm{T}}}}{\left(\frac{R_{\mathrm{AB}} y_{\mathrm{A}}}{w_{\mathrm{A}}^0} + \frac{y_{\mathrm{B}}}{w_{\mathrm{B}}^0}\right)^2} \tag{27}$$

where R_{AB} is the ratio of the Henry's constants, that is (a_1/b_1).

For each system, the sets of K_{A} and K_{B} values shows systematic (if only slight) differences. The procedure is then to fit each set of K_{A} and K_{B} values using (27). A *different* set of best-fitting parameters—w_{A}^0, w_{B}^0 and R_{AB}—would be expected for each perturbation gas. Consider that for a particular system, on average the set of K_{A} values is 1% greater than the set of K_{B} values. This *might* result in all three fitting parameters being 1% greater for K_{A} than for K_{B}. Alternatively, only two of the parameters might be greater for K_{A}, and the other less. It should be pointed out that the fitting of data using (27) is a rigorous test of the experimental data: this is because the pure-component amounts adsorbed are allowed to float, whereas in other fitting approaches the pure-component amounts are fixed by the results from the pure-component experiments.

5 Experimental data

The experimental data for this work is classified as Systems 1 to 4 and the details are shown in Table 1. For each system, the adsorbate gases are nitrogen and argon, and the adsorbent is 5A zeolite. The data for systems 1 to 3 was obtained using a glass column with an internal diameter of 4 mm and a length of 150 cm. The 5A zeolite was ordered as pellets and ground down to the size range of 500–710 mm, and the column was then filled with 18.8 g of packing. The variation between Systems 1 and 3 is due to the different values of column temperature (25 °C, 54 °C and 81 °C). For System 4, the column temperature is 35 °C—and significantly, a flow-resistance is placed downstream of the glass column. These systems have been selected because the column pressure drop (ΔP_{c}) is an important parameter with regard to the measured retention time: the value of ΔP_{c} increases steadily from Systems 1 to 3 as the column temperature is increased, and for System 4 there is a *sharp* increase in the "effective" value of ΔP_{c} when the flow-resistance is placed downstream of the column. System 4 is also distinctive because it involves a number of mixture perturbations, as well as the standard nitrogen and argon perturbations. The *variation* of ΔP_{c} in Systems 1 to 4 is required for Objective 2,

Table 1 Summary of details for each of the systems

System	Source	T_{C} (°C)	ΔP_{C} (bar)	P_{cmean} (bar)	c_{T} (mol/m^3)
1	Heslop (1993)	25	0.1	1.15	46.4
2	Heslop (1993)	54	0.12	1.16	42.7
3	Heslop (1993)	81	0.15	1.18	40.1
4	Heslop et al. (1998)	35	(0.6)	1.40	54.7

since this involves validating the relationship (Objective 1) between the measured retention time (t_{step}) and the column pressure drop (ΔP_{c}). The variation of the perturbation *composition* ($y^{\mathrm{p}}_{\mathrm{N2}}$) in System 4 is a more rigorous test of Objective 1. The *values* of ΔP_{c} in Systems 1 to 4 are *large enough* to ensure that the set of nitrogen-perturbation retention times is systematically greater than those for the argon perturbation. Each set of retention times is then used to try and predict the binary isotherms. Of course, each set (nitrogen and argon) will give different binary isotherm predictions, and this is a requirement for Objective 3. This would *not* be the case for a column with a much smaller value of ΔP_{c} since any systematic differences between the nitrogen-perturbation and argon-perturbation retention times would be lost in the experimental (random) errors.

The experimental data for Systems 1 to 3 are shown in Tables 2 to 4. The values of K_{N2} and K_{Ar} were obtained by substituting the measured retention times (t_{N2} and t_{Ar}) into (9). Note the units for K are (mL/g). These are preferred to m^3/kg because the factor of 1000 would make the numbers less convenient to manage. It can be seen that in each table, there is a reduction in the value of t_{g} with a greater amount of nitrogen in the mixture. This is due to the increasing main gas flow rate. The flow is set by a fixed pressure drop across a fixed resistance: the viscosity of nitrogen is about 20% less than that of argon. The entries in parentheses correspond to the cases where it was not possible to obtain a retention time with the respective perturbation. For example, if a nitrogen perturbation is added to a nitrogen main flow, there is no response in the composition signal. However, from the findings of (21), for a pure main gas, the composition retention time is independent of the perturbation composition.

It is not a trivial matter to determine the value of V_{g} and hence the values of t_{g}. The empty column has a volume of 18.9 mL. The voidage (the space between the pellets) is 0.376. However, there is also space *inside* the pellets. Let us assume that the pellets have the same voidage (0.376). Furthermore, there is around 2 mL of dead volume in the tubing and around 1 mL in the katharometer. This gives an estimated value of V_{g} of around 14.5 mL. To determine the composition retention time (t_{step}) it is necessary to measure an area of the TCD record and divide it by the difference between the initial and final baselines. For all the results, the detector signals were recorded on chart paper and this necessitated using a planimeter to measure the area and a ruler to measure the offset. The confidence limits in the values of t_{step} are estimated to be about ±1%.

Table 2 Measurements and calculations for System 1 at 25 °C

% N_2	t_{g} (s)	t_{N2} (s)	t_{Ar} (s)	K_{N2} (mL/g)	K_{Ar} (mL/g)	Ratio ($K_{\mathrm{N2}}/K_{\mathrm{Ar}}$)
0	49.3	470	(470)	9.96	9.96	1.00
10	48.4	429	425	9.21	9.11	1.01
25	47.0	353	351	7.63	7.58	1.01
50	44.5	257	254	5.59	5.52	1.01
75	41.9	185	180	4.00	3.86	1.03
90	40.3	144	144	3.02	3.02	1.00
100	39.1	(123)	123	2.51	2.51	1.00

Table 3 Measurements and calculations for System 2 at 54 °C

% N_2	t_{g} (s)	t_{N2} (s)	t_{Ar} (s)	K_{N2} (mL/g)	K_{Ar} (mL/g)	Ratio ($K_{\mathrm{N2}}/K_{\mathrm{Ar}}$)
0	45.3	242	(242)	5.05	5.05	1.00
10	44.3	225	222	4.76	4.68	1.02
25	45.9	207	206	4.10	4.07	1.01
50	42.8	159	159	3.17	3.17	1.00
75	39.1	119	118	2.37	2.36	1.00
90	38.1	102	102	1.95	1.95	1.00
100	37.1	(92)	92	1.73	1.73	1.00

Table 4 Measurements and calculations for System 3 at 81 °C

% N_2	t_{g} (s)	t_{N2} (s)	t_{Ar} (s)	K_{N2} (mL/g)	K_{Ar} (mL/g)	Ratio ($K_{\mathrm{N2}}/K_{\mathrm{Ar}}$)
0	45.5	162	(162)	3.01	3.01	1.00
10	43.9	152	149	2.90	2.82	1.02
25	42.0	134	134	2.57	2.57	1.00
50	39.4	111	111	2.14	2.14	1.00
75	36.4	90	89	1.72	1.70	1.01
90	34.5	78	77	1.47	1.45	1.01
100	35.6	(77)	77	1.37	1.37	1.00

The importance of System 4 deserves further explanation. As can be seen for Systems 1 to 3, the systematic differences between the retention times for the "standard" column are small. So in order to obtain an exaggerated effect, Heslop et al. (1998) repeated some results for the nitrogen–argon–5A zeolite system at 35 °C but with a capillary resistance downstream of the column. The effect of this resistance was to generate a much larger increase in the mean column pressure (P_{cmean}) when the perturbation gas was added to the column. When a perturbation flow is added to a main flow passing through a flow resistance, the increase in the *inlet* pressure is about *twice* that of the mean pressure (Mason and Buffham 1996b). This increase acts on the whole column, and so the value of P in (13) varies as shown

$$P \approx \frac{\Delta P_{\mathrm{c}}}{2} \to P \approx \frac{\Delta P_{\mathrm{c}}}{2} + \Delta P_{\mathrm{r}}$$

where ΔP_{r} is the pressure drop across a 20-cm length of tubing with a bore of 0.2 mm. The value of ΔP_{r} was measured to be 0.25 bar. Placing the resistance downstream of the column therefore changes the value of P by a factor of about six. The nitrogen and argon perturbation retention times are 204 and 191 seconds respectively—a much greater difference—confirming that the difference between the retention times is exaggerated by the inclusion of an extra resistance and the subsequent increase in the value of P. System 4 differs from Systems 1 to 3 in a number of ways: it involves a *single* main-flow composition and a *number* of perturbation (mixture) compositions varying from pure nitrogen to pure argon.

6 Processed results: determination of binary isotherms from retention times

The results for Systems 1 to 3 will be considered first. Figures 4 to 6 show the values of K_{N2} and K_{Ar} along with the curves using the best-fitting parameters. These figures show that (27) gives a good fit to the data. Table 5 shows the three best-fitting parameters for each of Systems 1 to 3. A sensible starting point is to consider the variation of the parameters with system temperature. As expected, the pure-component adsorbed amounts of nitrogen and argon decrease with increasing temperature. Furthermore, the ratios of the pure-component amounts (w) and the Henry constants (R)—where the ratio indicates nitrogen to argon—also decrease with increasing temperature: these are also shown in Table 5.

At this stage, the experimental data from this work can be compared with that from the literature. The only comparable literature data were obtained by Verelst and Baron (1985) who used a volumetric technique to determine pure and binary isotherms. Their results are summarised in Table 6. It is a little tricky to make comparisons between this work and the literature data for two reasons: the values of the fitting parameters for each perturbation gas are different, and the temperatures are slightly different in each investigation. Furthermore, it can be seen that the absolute values of the pure-component amounts adsorbed (mol/kg) are greater for this work than for the literature data. This may be in part due to the adsorbents having different binder amounts or different activities. In any case, the implication is that it would be better to examine the *ratio* of the pure-component amounts adsorbed, and these are shown in Fig. 8. Figure 8 shows that there is a systematic difference between our experimental data and the literature. The secondary y-axis of Fig. 8 shows the ratio of the Henry constants, and it can be seen that there is a similar systematic difference between our investigation and the literature. This will be considered in more detail in Sect. 7.

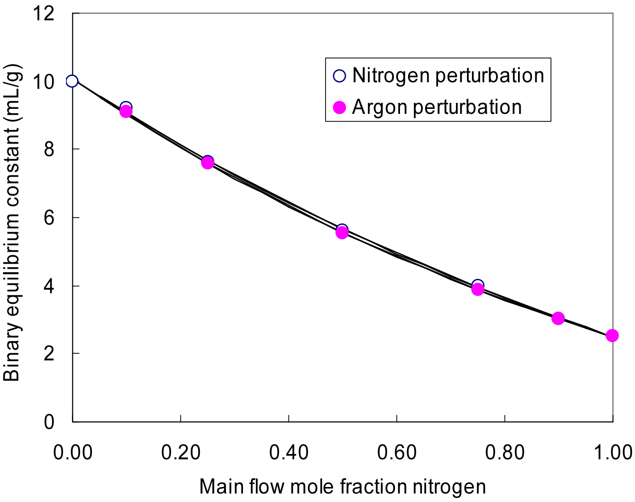

Fig. 4 Calculated values of K_{N2} and K_{Ar} for System 1 (25 °C) and best-fitting curves. The position of the curves indicates a systematic difference in the data

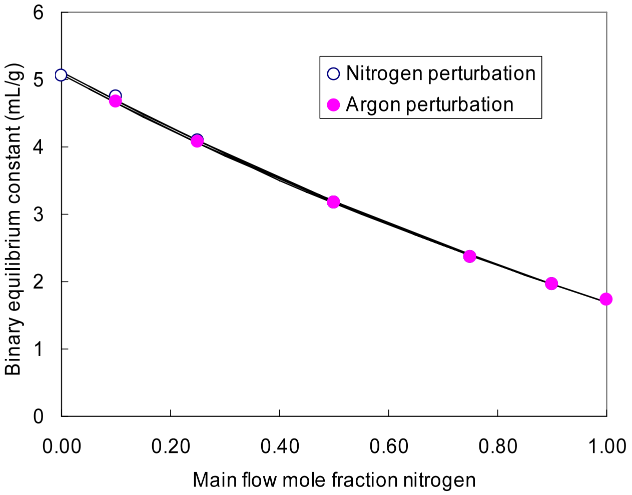

Fig. 5 Calculated values of K_{N2} and K_{Ar} values for System 2 (54 °C) and best-fitting curves. The nitrogen curve is now closer to the argon curve

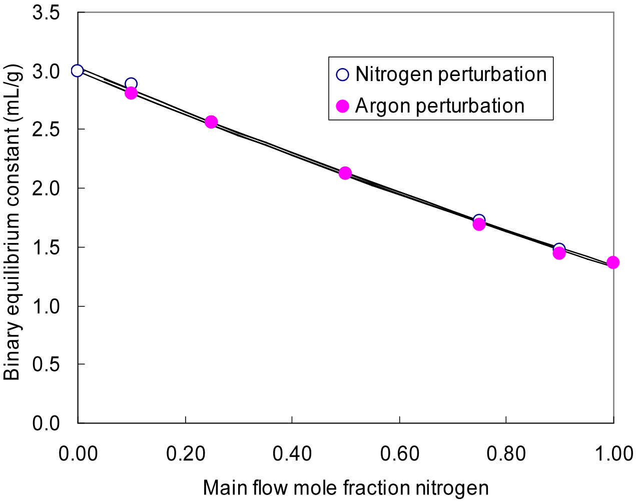

Fig. 6 Calculated values of K_{N2} and K_{Ar} values for System 3 (81 °C) and best-fitting curves. The two curves are now almost co-incident

Table 5 Parameters from fitting (27) to each set of retention times

System: (pert)	Temp. (°C)	R_{N2Ar}	w^0_{N2} (mol/kg)	w^0_{Ar} (mol/kg)	$\frac{w^0_{\mathrm{N2}}}{w^0_{\mathrm{Ar}}}$
1:(N_2)	25	3.37	0.389	0.139	2.81
1:(Ar)	25	3.28	0.378	0.142	2.66
2:(N_2)	54	2.62	0.190	0.083	2.28
2:(Ar)	54	2.58	0.188	0.084	2.23
3:(N_2)	81	2.11	0.114	0.058	1.98
3:(Ar)	81	2.12	0.113	0.057	2.00

Table 6 Summary of data from literature (Verelst and Baron 1985)

Temp. (°C)	P_{cmean} (bar)	R_{N2Ar}	w^0_{N2} (mol/kg)	w^0_{Ar} (mol/kg)	$\frac{w^0_{\mathrm{N2}}}{w^0_{\mathrm{Ar}}}$
25	1.03	3.54	0.327	0.111	2.95
47	1.00	2.85	0.195	0.077	2.53
75	1.02	2.43	0.111	0.048	2.31

Next, the results from this work are considered in more detail, in particular the differences between the three best-fitting parameters for each perturbation gas. For Systems 1 and 2, both ratios (R and w) are higher for the nitrogen perturbation gas. For System 3, however, the parameters are almost identical. For System 1, the retention times differ by, on average, 1%. However, the two ratios (R and w) differ by 3% and 6% respectively. This shows that using the binary-Langmuir approach of (27), the retention times need to be almost *identical* for the best-fitting parameters to agree to better than 1%: the method is very sensitive to data input. This is not surprising in view of the details of the procedure for the binary-Langmuir approach: the pure-component amounts adsorbed are not specified but allowed to float according to the data. A less-rigorous approach would be a one-parameter procedure, in which the pure-component amounts are specified.

Finally, the results for System 4 are considered. The data is shown plotted in Fig. 9 and the reason for this inclusion is to test (15) in a rigorous manner. Note that the plot is of K_{step} against the *inverse* of $(y^{\mathrm{P}}_{\mathrm{N2}} - y^0_{\mathrm{N2}})$. This means that the two middle points correspond to the pure-component perturbations, and the other six points correspond to various mixture perturbations flows. According to the form of (15), for a fixed main-gas composition, the plot should be linear with gradient PG. This is apparently confirmed in Fig. 9, with just one point deviating from the straight line.

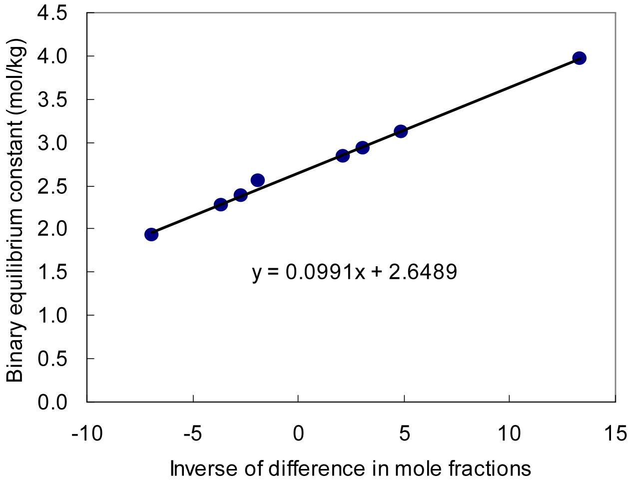

Fig. 7 Calculated K_{step} values for a 53% nitrogen main flow. The linearity of the plot confirms the variation predicted by (15)

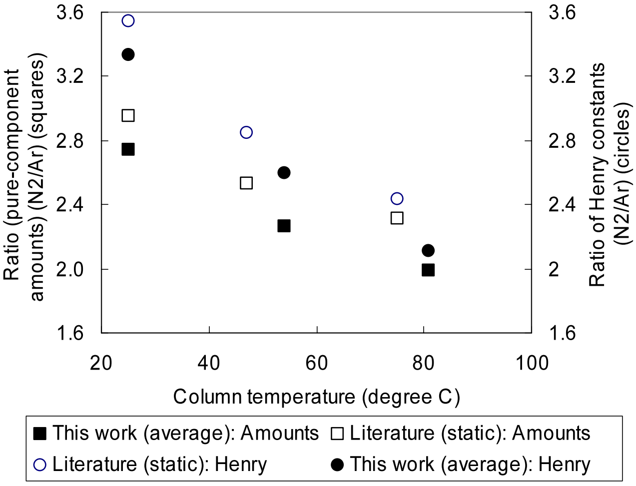

Fig. 8 Comparison of isotherm predictions from this work: "*average*" refers to the average of the fitting parameters obtained from the nitrogen and argon sets of retention times

7 Discussion

For convenience, this is divided into five parts. The first part deals with the practical implications for the experimentalist regarding the determination of binary adsorption isotherms. For example, if the values of t_{step} are 200 and 205 seconds for the two perturbations, what is the value that corresponds to the (ideal) column with a zero pressure drop? This is important when a set of retention times is to be used to determine the binary isotherms, and is based on Objective 1. The second part deals with the validation of the complete solution given by (15): for example, can it be proved that the value of t_{step} for nitrogen is always greater than for argon? This is based on both Objectives 1 and 2. The third part looks in more detail at System 4, and the effect of placing a flow resistance downstream of the column:

this is to simulate a column having a much larger pressure drop. Once again, this is also based on Objective 1; however, confirmation of the theory requires that a plot of retention time against some function of the perturbation composition *should be linear*. The fourth part involves how the *actual* retention times for Systems 1 to 3 are processed to give the binary isotherm predictions: the nitrogen and argon retention times will give different predictions. This is based on Objective 3. The final part is a comparison with literature for the same adsorbent. This is also based on Objective 3, but looks at various reasons why the results from this investigation and from literature might not agree exactly.

1. Equation (18) has a potentially useful form since it relates the required constant-pressure value (K_{CP}) to the experimental values obtained from the A and B perturbations (K_{A} and K_{B}). This is interesting because the extra term in square brackets involves the variation of viscosity with composition. This would be zero for a system in which the viscosity is (almost) independent of composition. In order to show how simplification might be achieved, it is helpful to divide by K_{A} as shown in (28).

   $$\frac{K_{\mathrm{CP}}}{K_{\mathrm{A}}} = y_{\mathrm{A}}^{0}\frac{K_{\mathrm{B}}}{K_{\mathrm{A}}} + y_{\mathrm{B}}^{0} - \left[y_{\mathrm{A}}^{0} y_{\mathrm{B}}^{0}\frac{\Delta K}{K_{\mathrm{A}}}\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}\right](y_{\mathrm{A}}^{0})\right] \quad (28)$$

   A typical value of the normalised gradient for the nitrogen/argon system is 0.2. Consider a 50% mixture for which the fractional difference between K_{A} and K_{B} is 0.01—typical of the results in our investigation. This means that the first two terms on the right-hand-side of the equation sum to 1.005. The correction term in the square brackets is −0.0005, which means that this can be ignored. Consider now a system with a much *larger* column pressure drop, for which the fractional difference between K_{A} and K_{B} is, say, 0.1. Here, the first two terms on the right-hand-side sum to 1.05, and the viscosity correction term is equal to −0.005. Hence, the viscosity term can be safely ignored, and that K_{CP} is a simple weighted function of the values of K_{A} and K_{B} obtained from a column with a finite pressure drop:

   $$K_{\mathrm{CP}} \approx y_{\mathrm{A}}^{0} K_{\mathrm{B}} + y_{\mathrm{B}}^{0} K_{\mathrm{A}}$$

   So, for a 75% A mixture in which the values of t_{step} are 110 and 100 seconds respectively, the value of t_{CP} (required to determine the value of K_{CP}) is actually 102.5 seconds.
2. In order to consider the difference in retention times for each perturbation gas, it is helpful to first subtract (17) from (16) to give the fractional difference shown in (29).

   $$\Delta K = K_{\mathrm{A}} - K_{\mathrm{B}}$$

   $$\rightarrow \frac{\Delta K}{K_{\mathrm{A}}} = \left[(y_{\mathrm{A}}^{0} y_{\mathrm{B}}^{0})\frac{1}{P}\frac{K_{\mathrm{CP}}}{G} + (y_{\mathrm{A}}^{0} y_{\mathrm{B}}^{0})\left[\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}y_{\mathrm{A}}}(y_{\mathrm{A}}^{0})\right] + y_{\mathrm{A}}^{0}\right]^{-1} \quad (29)$$

   For the data of System 1, the fractional value of ΔK is about (+) 0.01. From (13), the value of P is around 0.04. By inserting these values into (29), the first term in the square brackets is dominant and that the value of the ratio of K_{CP} to G is around 15. It is helpful to consider this ratio in more detail. For the 50% main flow, this is written as:

   $$\frac{K_{\mathrm{CP}}}{G} = 2 \times \frac{\left(\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{A}}} + \frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right) - \frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{B}}} - \frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{A}}}}{\left(\frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{A}}} - \frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right) + \frac{\partial w_{\mathrm{A}}}{\partial c_{\mathrm{B}}} - \frac{\partial w_{\mathrm{B}}}{\partial c_{\mathrm{A}}}}$$

   $$\rightarrow \frac{K_{\mathrm{CP}}}{G} = 2 \times \frac{[(+)+(+)]-(-)-(-)}{[(+)-(+)]+(-)-(-)}$$

   The first two partial gradients in both numerator and denominator are *positive* and the second two are *negative*—the latter are termed cross-term. Typically, the magnitudes of the cross terms are smaller than the magnitude of the first partial derivatives. Consider a typical system for which $\partial w_{\mathrm{A}}/\partial w_{\mathrm{A}}$ is assigned an arbitrary value (+4) and $\partial w_{\mathrm{B}}/\partial w_{\mathrm{B}}$ is assigned a different arbitrary value (+2). This would explain why the ratio of K_{CP} to G is positive: nitrogen is the more-strongly adsorbed component, and so the retention time and subsequent value of K_{N2} is greater than that for K_{Ar}. Substituting, the ratio of (K_{CP}/G) is necessarily greater than 6. Consider further that the cross-terms ($\partial w_{\mathrm{A}}/\partial w_{\mathrm{B}}$ and $\partial w_{\mathrm{A}}/\partial w_{\mathrm{A}}$) are assigned an arbitrary value of (−1). These change the ratio (K_{CP}/G) to 8, close to the calculated value of 15. Systems 2 and 3 involve higher temperatures. This will affect (29) in two ways: the value of P will *increase* with temperature and the values of K_{CP} and G will both *decrease* with temperature. From Tables 3 and 4, it is difficult to make comparisons between K_{N2} and K_{Ar}, because the values of t_{step} are smaller and so any differences more difficult to ascertain. However, the fractional value of ΔK decreases to about 0.004 for the higher temperatures. This implies that the ratio (K_{CP}/G) will fall with temperature. Certainly, all four partial gradients will fall with increasing temperature: these findings are not unreasonable since the sum of two partial gradients will fall greater than the difference of two partial gradients.
3. The inclusion of System 4 (shown in Fig. 7) is instructive for two reasons. First, the column has a much larger “effective” pressure drop, meaning that any differences in the retention times will become more apparent. Second, it involves a number of perturbations of

different composition, not just the two pure perturbation gases. This allows to test (15), since a plot of K_{step} against the inverse of $(y_A^p - y_A^0)$ should yield a straight line.

$$K_{\text{step}} = K_{\text{CP}} + PG\left[\frac{1}{\mu}\frac{d\mu}{dy_A}(y_A^0)\right] + PG\frac{1}{y_A^p - y_A^0}$$
$$\rightarrow y = mx + c$$

This is clearly shown in Fig. 7. The next step is to validate the gradient in Fig. 7, by comparison with System 1. The carrier mixture composition is close to 50% (53% actually) and the temperature (35 °C) is fairly close to that for System 1 (25 °C). From discussion point 2, (29) can be simplified to:

$$\Delta K = K_A - K_B \rightarrow \frac{\Delta K}{K_A} \approx \left[(y_A^0 y_B^0)\frac{1}{P}\frac{K_{\text{CP}}}{G}\right]^{-1}$$
$$\rightarrow \frac{\Delta K}{K_A} \propto P$$

This would suggest that the fractional value of ΔK at a particular main-flow composition should be proportional to the value of P. In the standard column arrangement, the value of P is around 0.05 and the fractional value of ΔK is around 0.01 (the 1% difference). Placing the resistance downstream of the column changes the value of P to around 0.3. This might be expected to increase the fractional value of ΔK from around 0.01 to around 0.06. The actual values of K_{N2} and K_{Ar} from Fig. 7 are 2.83 and 2.56 respectively, a fractional (ΔK) of around 0.1. This is good agreement given the number of assumptions.

4. This part considers in more detail the binary isotherms obtained by substituting each set of K_{step} values into (27). An appropriate starting point is the data for System 1. Even though the retention times for nitrogen are on average 1% higher than those for argon, the best-fitting parameters vary by considerably more: the value of R_{N2AR} for the nitrogen data (3.37) is 3% greater than the value for the argon data (3.28). Furthermore, the value of w_{N2}^0 for the nitrogen data (0.389) is 3% *greater* than that obtained for the argon data, and conversely the value of w_{Ar}^0 for the nitrogen data (0.139) is 2% *less* than that obtained for the argon retention times. So, a 1% variation in the retention times changes the best-fitting parameters by +3%, +3% and −2%. This is not surprising: the form of the binary-Langmuir isotherm proposed by Buffham et al. (1999) allows the pure-component amounts adsorbed to float. In other fitting routines, the pure-component amounts adsorbed are usually specified. The conclusion is that a corrected set should be used to allow for the fact that the column concentration (c_T) is changed by the perturbation flow. For example, for the 50% mixture the required value of t_{CP} is 255.5 s (rather than 254 or 257 s) and for the 75% mixture the required value of t_{CP} is 181 s (rather than 185 or 180 s).
5. Caution should be exhibited in comparing the results with literature, because there is only one set of published work (Verelst and Baron 1985). Furthermore, although the adsorbent (5A zeolite) is the same, there will be obvious differences in the binder and amorphous material contents. However, it is not unreasonable to make comparisons of the ratios of the pure-component amounts adsorbed $(w_{\text{N2}}^0/w_{\text{Ar}}^0)$ and the Henry constants (R_{N2Ar}): these should not be affected by variations in binder content. The comparisons are represented in Fig. 8. The solid symbols refer to the isotherms determined from this investigation, and the empty symbols refer to the literature data. It can be seen that both (R_{N2Ar}) and $(w_{\text{N2}}^0/w_{\text{Ar}}^0)$ are lower than the literature across the whole temperature range. An important parameter is the unretained pulse time (t_g), the value of which is fixed by the column flow rate and the *estimated* empty volume (V_g) of 14.5 mL (for which there is some doubt). For System 1 at 25 °C, the R and w ratios for the nitrogen perturbation (3.37 and 2.81) are greater than those for the argon perturbation (3.28 and 2.66). Consider that the nominal value of 14.5 mL is subject to error. A *reduction* by about 1 mL would *reduce* the t_g values by about 2 seconds which would *increase* the values of R and w to approach the literature values (3.54 and 2.95). For systems with low/medium adsorption, the value of t_g is important because it is significant compared to t_A and t_B. This would not be an issue for high-adsorption systems, with much greater values of t_A and t_B: for example hydrocarbons on 5A zeolite.

8 Conclusions

The composition retention time is an important parameter for the characterisation of adsorption in binary systems. For experimental arrangements involving the addition of a pulse of gas, the theory is well-understood: the pulse volume should be as small as possible, and the retention time is related to the binary isotherm gradients at the composition of the main (carrier) flow. However, for arrangements where a small flow is added, there is no corresponding theory in the literature. The change in flow causes a small increase in column pressure, and the retention time will depend on the perturbation gas. The first objective of this work has been to obtain the complete solution which shows how the composition retention time for a particular main-flow composition depends on the composition of the perturbation gas, the column pressure drop and the variation of viscosity with composition for the binary mixture. This solution involves a parameter (termed G) that involves the four partial isotherm gradients and the main flow composition. For a single-component main flow *only*, the retention time is shown to be *independent* of the perturbation composition.

The second objective has been to validate the expressions for the retention time using experimental data. For the nitrogen–argon–5A zeolite system at 25 °C, the composition retention times for the two pure-component perturbations differ by around 1%—these are for a column pressure drop (ΔP_c) of around 0.1 bar. The complete solution suggests that the % deviation between the two pure-component retention times should be proportional to the column pressure drop; and indeed, for a ΔP_c value of around 0.6 bar, the deviation is about 5%. For the majority of the main flow compositions, the retention time obtained for the nitrogen perturbation (the more-adsorbed component) is greater than that obtained for the argon perturbation. This is confirmed in the complete solution by the parameter that involves the partial gradients of the adsorption isotherms.

The third objective has been to assess how the retention times are used in a procedure to determine the binary adsorption isotherms. What is required is the composition retention time that *would be* obtained for a column with a *zero* or very small pressure drop: this is the value required for one of the various procedures, in which a set of retention times is used to predict the binary adsorption isotherms at the system temperature and pressure. In this work, we have used a procedure based on the binary-Langmuir approach, in which the fitting parameters are the pure-component amounts adsorbed and the ratio of the Henry constants. As expected, using the nitrogen-perturbation and argon-perturbation set of retention times will give a *different* set of fitting parameters since at each carrier composition, the nitrogen-perturbation retention times are about 1% greater than those for argon. Indeed, even though the variation in retention times is 1%, the ratios of the Henry constants and pure-component amounts adsorbed differ by much more: 3 and 6% respectively. For a typical experimental investigation of a binary system, it might be required to determine these ratios to say 1%—and for this case, it is *especially important* to obtain the zero pressure-drop value of the retention time. This is the practical significance of this work.

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