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4 **Measurement of adsorption of a single component from the liquid phase:**
5 **modelling investigation and sensitivity analysis**
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9

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20 **Keywords:** adsorption, ethanol, liquid, flow measurement, theory
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22

23 **Abstract**
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25
26 In this work, we consider an alternative approach for the measurement of adsorption from the
27 liquid phase. Consider a mixture consisting of a non-adsorbed component (B) and an
28 adsorbed component (A) present at some low concentration. Initially, a feed of component B
29 only flows through a column packed with an adsorbent. Then, the feed is switched to the
30 mixture of A and B. As soon as the mixture enters the column, there will be a reduction in the
31 outlet flow rate as component A leaves the liquid phase and passes into the adsorbed phase.
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33 There are three stages to this work. The first is to develop overall and component balances to
34 show how the amount adsorbed of component A can be determined from the variation in the
35 column outlet flow rate. The second is to determine the actual variation in the column outlet
36 flow rate for both plug flow and axial-dispersed plug flow. The final stage is to consider the
37 suitability of a gravity-fed system to deliver the feed to the column. An analysis of the results
38 shows that the experimental arrangement should be able to accurately monitor adsorption
39 from the liquid phase where the mass fraction of the solute is of the order of 1%: the limiting
40 experimental factor is how constant the volumetric flow rate of the liquid feed can be
41 maintained.
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Introduction

In recent years, there has been an increase in the number of applications, publications and patents for adsorption in the liquid phase. This is in part due to the increasing number of purification applications, where the requirement is to remove a low concentration of a component which is capable of adsorption. One application is the removal of water from organic solvents. Lau et al. (2004) used a packed column of spherical beads of 3A zeolite to dry an ethanol solution containing 3.2 % of water. The authors used titration to determine the concentration of water in ethanol and concluded that the application of oscillatory flow resulted in improved column performance. Environmental applications include the removal of phenol from water (Roostaei and Tezel, 2004) and naphthalene from water (Chang et al., 2004). In the former, the starting solution was phenol in water at a concentration of 200 ppm.

For the design of such purification and separation processes, a key parameter is the adsorption isotherm for a particular solute and material. This is conveniently written as

$$q = f(c) \quad (1)$$

where q is the adsorbed-phase concentration (for which convenient units are say mg/g) and c is the concentration of the solute in the liquid phase (for which convenient units are say g/L).

The various experimental methods are covered in a recent review by Seidel-Morgenstern (2004). These can be classified into two broad categories: static and dynamic. In the former, an amount of adsorbent is contacted with a known volume (V) of solution with an initial concentration (c_{start}) of the solute. The concentration is then monitored until the equilibrium value (c_0) is attained. A material balance then gives the amount adsorbed

$$\Delta m_{\text{ads}} = V(c_{\text{start}} - c_0) \quad (2)$$

assuming that, initially, the adsorbent is clean of the adsorbed component. The value of Δm_{ads} is then used to give the point on the isotherm, that is $q(c_0)$. There is a modification to this

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3 method which involves regenerating the adsorbent with a flow of eluent. This is continued
4 until the concentration of the solute in the eluent reduces to zero. The total volume of eluent
5 is collected, mixed and analysed to give an “average” solute concentration. This approach is a
6 double-check on the amount adsorbed: assuming that regeneration is complete, the material
7 balance should then give the same value of Δm_{ads} determined from Equation (1). The whole
8 procedure is then repeated with a different starting concentration (c_{start}) which gives a different
9 final (or equilibrium) concentration (c_0). There are two drawbacks with the static approach:
10 the time and material requirements can be prohibitive, and the equilibrium concentration (c_0)
11 is the value at the end of the experiment rather than at the start.
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25 For the dynamic category, the adsorbent is contained as a packed column with a solution
26 containing the solute as a feed. Then, at time zero, some change is made to the feed
27 concentration of the solute. Information on the adsorption isotherm is then obtained from the
28 variation with time of the solute concentration in the outlet flow – that is, $c(t)$. This “change”
29 is conveniently obtained by increasing the feed concentration from zero to a value of c_0 – the
30 variation of $c(t)$ would then be the breakthrough curve. Alternatively, the change might be to
31 reduce the feed concentration from c_0 to zero – this variation of $c(t)$ is sometimes known as
32 the washout curve. The use of a step-change in concentration is termed frontal analysis (FA),
33 for which the equilibrium value of q is obtained from
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$$q = \frac{Q \int_0^{\infty} [c_0 - c(t)] dt - Vc_0}{W} \quad (3)$$

46 where V is the total empty space in the system between the valve and detector, Q is the
47 volumetric flow rate and W is the mass of adsorbent. The selection of the correct value of V is
48 especially important when the solute is not strongly adsorbed and the integral is not large
49 (Gritti and Guiochon, 2005a). Furthermore, the value of Q should be maintained as constant
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4 as possible (Gritti and Guiochon, 2005b): an increase in flow rate gives a slight increase in the
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6 amount adsorbed because of the increase in column pressure. An advantage of FA is that it is
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8 based on a material balance and is independent of any mass-transfer limitations or axial
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10 dispersion.

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13 The perturbation method is a variation on the FA method. This involves setting the feed
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15 concentration to a particular value (c_0), and then adding “small” pulses of increasing size.
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17 From this set of results, the isotherm gradient is determined at the value of c_0 . The whole
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19 procedure is then repeated at various values of c_0 , starting at zero. The complete isotherm is
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21 finally obtained by integration of the set of gradients.
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25 Consider now an “efficient” adsorption column: this is defined as a column in which the mass
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27 transfer is rapid and axial dispersion can be ignored. Consider now a pulse injection of the
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29 adsorbed component: this is obtained by increasing the inlet concentration of the solute from
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31 zero to a finite value and then back to zero. In this case, the passage of the pulse through the
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33 column will consist of a “sharp” front and a “dispersive” front. The degree of dispersion is
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35 determined by the curvature of the isotherm; each point (c) on the isotherm will travel at a
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37 speed determined by the isotherm gradient. This is termed elution by characteristic point
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39 (ECP), the advantage of which is that a significant part of the isotherm can be determined
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41 from a single experiment.
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46 The method proposed in this paper is distinctive in that our intention is to measure the
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48 adsorption isotherm by monitoring the variation in the volumetric flow rate leaving the
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50 column rather than by monitoring the solute concentration. There are a number of reasons
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52 why we are proposing such a method. First, to date all previous work in the groups at
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54 Strathclyde, Loughborough and Teesside has been in the gas phase. This is therefore a logical
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56 extension to the liquid phase. Second, our expertise is a method to measure small changes in
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58 flow rate and the application to material balances in various types of system. The method can
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4 be summarised by considering that a flow resistance is placed downstream of the adsorption
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6 column. Assuming that the flow regime is laminar, the pressure drop (ΔP) is related to the
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8 volumetric flow rate leaving the adsorption column (Q) by the Hagen-Poiseuille equation
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$$\Delta P = k\mu Q \quad (4)$$

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14 where μ is the viscosity and k is a tubing constant. It is helpful at this stage to consider an
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16 order of magnitude comparison between gas and liquid systems. Consider the adsorption of a
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18 component (solute) present at say 1% in a non-adsorbed mobile phase: in each case, there will
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20 be a reduction in the column outlet flow rate as the component passes leaves the mobile phase
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22 and passes into the adsorbed phase. The volume of a gas is typically three orders of
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24 magnitude greater than a liquid, however the viscosity of a liquid is typically two orders of
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26 magnitude greater than a gas. This would suggest that the application of Equation (4) to the
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28 measurement of changes in liquid flow rate due to adsorption might only be an order of
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30 magnitude less sensitive than for gases – which might be challenging – but is certainly worthy
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32 of further investigation.
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38 The implication of trying to monitor adsorption from the column outlet flow rate in a liquid
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40 system is that the volumetric flow rate of the feed should be kept as constant as possible,
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42 especially where the solute is present at low concentrations. Gritti and Guiochon (2004)
43
44 carried out an HPLC investigation on the adsorption of phenol using a mixture of water and
45
46 methanol as the mobile phase. They found that the fluctuation in the pumping system was
47
48 about 0.1%, for a feed flow rate of 1 mL/min. In our case, by not operating under pressure we
49
50 have the option of delivering the feed flow using an alternative method. The obvious solution
51
52 might be some sort of pump capable of operating at low flow rates: that is, the syringe pump
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54 or piston pump. However, there are a number of potential problems with such a pump. First
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56 we are limited by the amount of liquid placed initially in the syringe, which could pose a
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58 problem if we require the flexibility of operating at higher flow rates and longer experimental
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4 times. Second, it is essentially a mechanical device in which the plunger is pushed in at a
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6 constant rate by a gear arrangement. Third, even if the gear arrangement is perfect, it
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8 requires a *perfect* cylinder to deliver a constant flow: this is a uniform diameter across the
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10 length of the cylinder.

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13 There are three objectives to this research.

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16 1. The first objective is to carry out a material balance on the column and to illustrate how
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18 the amount adsorbed in an experiment can be obtained from the variation in the volumetric
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20 flow rate leaving the column and known physical properties. Krige and Pretorius (1965)
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22 presented an analysis for the flow rate changes that occur due to the adsorption of a solute and
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24 specifically stated that the analysis could also be applied to the liquid phase. However, we
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26 can find no record in the literature of any investigation of flow-rate changes in the liquid
27
28 phase. So, this is very much a pioneering – and challenging – investigation.

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30
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32 2. The second objective is to model the adsorption system and predict the actual variation
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34 in column outlet flow rate as the composition front enters, travels through and leaves the
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36 column. The shape of the composition front monitored by a detector at the outlet of the
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38 column is well-established in the literature for all types of adsorption system – plug flow,
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40 dispersed plug-flow. However, there is no such literature for the variation in column flow
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42 rate. We only know that the column outlet flow rate will drop as the front enters the column,
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44 and return to the original baseline as the front leaves the column: this would give, perhaps, a
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46 bath-shaped profile.

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50 3. The third objective is to assess a possible experimental arrangement capable of detecting
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52 the changes in flow rate due to adsorption. Here, we consider a gravity-driven system in
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54 which a constant head of liquid is maintained across an arrangement of flow resistances.
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56 Much of the literature involves the use of gravity to drive liquid flows through a flow
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58 resistance in order to measure the viscosity. However, the design is such that the liquid level
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4 and the flow rate are not constant but decrease with time, for example in the determination of
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6 the viscosity of water at different temperatures (Digilov and Reiner, 2007). Our experimental
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8 arrangement will be a variation on the gravity-fed system in which the volumetric flow rate
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10 *should remain* constant during the experiment. There are three reasons for this choice. First,
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12 it is a research area for which there is limited published work. Second, it is a low-cost and
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14 robust arrangement that can be readily and easily constructed from available equipment.
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16 Third, by monitoring the pressure signal we will know instantly whether the column is
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18 saturated and the outlet flow is indeed constant.
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23 **Theory of new method**

24 ***Overall material balance on column***

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26 Consider the schematic experimental arrangement shown in Figure 1 which consists of an
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28 adsorption column, a length of *empty* tubing of zero resistance and a length of *resistance*
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30 tubing. For the sake of simplicity, we consider a binary system of components A and B.
31
32 Component B is non-adsorbed – and is the equivalent of the “carrier” in gas chromatography
33
34 – while component A is capable of adsorption. Initially, the flow through the system is pure
35
36 component B at a fixed volumetric value of $Q(0)$. Then, a step change is made in the
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38 composition of the feed such that the mass fraction of component A takes a value x_A . Figure 1
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40 shows the progress of the composition front through the system. The basic material balance is
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42 given by
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$$50 \text{ in} = \text{out} + \text{accumulation}$$

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52 In a time interval dt , the total mass entering the system is equal to the total mass leaving plus
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54 the accumulation terms in the adsorbed and liquid phases. This can be written as
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56

$$57 Q(0)\rho_{\text{feed}}dt = Q(t)\rho(t)dt + (dm_A)_{\text{ads}} + (dm_A)_{\text{liq}} + (dm_B)_{\text{liq}} \quad (5)$$

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4 where ρ_{feed} is the density of the feed mixture and $\rho(t)$ is the density of the outlet at time t .
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6 This is initially ρ_B (pure-component B) until breakthrough of the concentration front. Note
7
8 that the presence of the delay volume ensures that for the duration of the experiment, pure
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10 component B is located in the measurement resistance. This can also be written as
11
12

$$13 \quad [Q(0) - Q(t)] \rho_{\text{feed}} dt + Q(t) [\rho_{\text{feed}} - \rho(t)] dt = (dm_A)_{\text{ads}} + (dm_A)_{\text{liq}} + (dm_B)_{\text{liq}} \quad (6)$$

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15
16 The second term on the left-hand side is equal to the two accumulation terms in the liquid
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18 phase. This allows Equation (6) to be simplified to
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$$21 \quad [Q(0) - Q(t)] \rho_{\text{feed}} dt = (dm_A)_{\text{ads}} \quad (7)$$

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24 which can then be integrated to obtain the amount adsorbed over an experiment.
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26

$$27 \quad (\Delta m_A)_{\text{ads}} = \rho_{\text{feed}} \int_0^{\infty} [Q(0) - Q(t)] dt \quad (8)$$

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32 The value of the integral can be simply determined from the variation of the outlet flow rate
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34 with time. The use of infinity as a limit of integration requires further explanation: this simply
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36 means the time taken to reach the new steady state in the column. The advantage of this
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38 continuous monitoring is to ensure that the new steady state is *definitely* attained in the
39
40 column. Consider that the first experiment is carried out with a mass fraction of component A
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42 of 0.01. The whole procedure would then be repeated with mass fractions of 0.02, 0.03 and so
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44 on up to say 0.1. Note that the value of ρ_{feed} would be different for each mixture, although
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46 this type of information is readily available from the literature. An important consideration at
47
48 this stage is the heat of reaction and the implications for Equation (8). Assuming the system
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50 temperature can return to the starting value before the composition front leaves the delay
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52 volume, this should ensure that the material balance is *not* affected by any temporary increase
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54 or reduction in temperature.
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4 We now return to the evaluation of the integral, which will have the dimensions of volume.

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6 This could be evaluated with a direct-reading meter, but for precise work this is best achieved

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8 by measuring the pressure drop across the flow resistance indicated in Figure 1. Writing

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10 Equation (4) for the initial situation

$$11 \quad P_2(0) - P_3 = k_F \mu_B Q(0) \quad (9)$$

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16 and then for the situation at any time t , we have

$$17 \quad P_2(t) - P_3 = k_F \mu_B Q(t) \quad (10)$$

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22 Equations (9) and (10) can be substituted into (8) to give

$$23 \quad (\Delta m_A)_{\text{ads}} = \frac{\rho_{\text{feed}}}{k_F \mu_B} \int_0^{\infty} [P_2(0) - P_2(t)] dt \quad (11)$$

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29 Therefore, the amount adsorbed during the experiment is determined by monitoring the

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32 variation of the pressure $P_2(t)$ with time, the density of the mixture, the viscosity of

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34
35 component B and a constant dependent on the dimensions of the tube.

36 37 **Material balance on component A**

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40 The material balance for a non-reaction system is given by

$$41 \quad \text{in} = \text{out} + \text{accumulation}$$

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45 In a time interval dt , the amount of component A entering the system is equal to the total mass

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48 leaving plus the accumulation terms in the adsorbed and liquid phases. This can be written as

$$49 \quad Q(0) c_0 dt = Q(t) c(L,t) dt + (dm_A)_{\text{ads}} + (dm_A)_{\text{liq}} \quad (12)$$

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52
53 where $c(L,t)$ is the liquid-phase concentration of component A leaving the column. If we

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56 consider a time *before* the start of breakthrough of component A, then the first term on the

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59 right-hand side becomes zero, and we can rearrange to a more convenient form

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$$\frac{(dm_A)_{\text{ads}}}{dt} + \frac{(dm_A)_{\text{liq}}}{dt} = Q(0) c_0 \quad (13)$$

This means that the sum of the two differential terms must be zero. We can also rearrange Equation (7) to give the differential balance on the total amount adsorbed in the column

$$\frac{(dm_A)_{\text{ads}}}{dt} = [Q(0) - Q(t)] \rho_{\text{feed}} \quad (14)$$

We assume equilibrium between the amount of A in both phases, in which case the ratio of the two differential terms is equal to a constant: this means that *before* the start of breakthrough of component A, value of $Q(t)$ must remain at a constant value. This is an important finding, since it helps to determine the variation of the column outlet flow rate.

Relation of variation in flow rate to concentration front

It is helpful to start by considering Figure 2 which shows the passage of a concentration front through an adsorption column. This is a special case in which the shape and width of the front remains constant. In practical terms, such a concentration front might be obtained by adding a small flow of the adsorbed component A into a non-adsorbed liquid, and allowing the flow of component A to increase linearly with time until the required composition. We know from the previous sub-section that while the concentration front is contained *entirely* within the column, the column outlet flow rate will remain at a *constant value*. For the sake of convenience, this will be termed the plateau value (Q_{plat}). However, as soon as the front reaches the end of the column – this is shown as the fifth series (dotted line) in Figure 2 – the column outlet flow rate will start to increase. This is the *start* of the breakthrough which is complete by the sixth series. By this time, the outlet flow rate will have returned to the original value of $Q(0)$.

We are also interested to determine the *actual* variation in the column outlet flow rate – that is $Q(t)$ – at breakthrough of the concentration front. This will be important in the next section,

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4 as we will be interested to determine the variation in $Q(t)$ for a number of concentration-front
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6 shapes. From intuition and observation, we know that the variation of $c(t)$ and $Q(t)$ tend to
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8 occur in tandem. During breakthrough, the value of $Q(t)$ is greater than Q_{plat} because of
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10 component A leaving the adsorbed phase and entering the liquid phase. This means that we
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12 can state that
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$$14 \quad Q(t) - Q_{\text{plat}} \propto Q(t) c(t) \quad (15)$$

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18 This can be written at any time t , and at the completion of breakthrough. The two equations
19
20 are then combined to give
21

$$22 \quad \frac{c(t)}{c_0} = \frac{Q(t) - Q_{\text{plat}}}{Q(0) - Q_{\text{plat}}} \left[\frac{Q(0)}{Q(t)} \right] \quad (16)$$

23
24
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26 This is important since it indicates that the shape of the concentration front is almost the same
27
28 as the shape of the variation of $Q(t)$ during breakthrough.
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32 ***The ideal variation in flow rate***

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35 Before the modelling section, it is first helpful to examine the “ideal” variation of flow rate
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37 leaving the column. In order to streamline explanations, it is helpful to employ a parameter
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39 (r), which is the ratio of the flow rate leaving the column at time t , to the initial value:
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41
42

$$43 \quad r = \frac{Q(t)}{Q(0)} \quad (17)$$

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45
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47 We now consider the properties of the feed. Consider first a *batch* system of components A
48
49 and B. Assuming these components form an ideal mixture, the volume of the mixture (V) can
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51 be written in terms of the specific volumes and masses of the two components by
52
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$$54 \quad V = m_A v_A^0 + m_B v_B^0 \quad (18)$$

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4 where the superscript 0 refers to the property of the pure liquid at the temperature and
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6 pressure of the system.
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9 Consider now a situation in which component A is removed from the mixture, as would be in
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11 the case of contact with an adsorbent of high affinity. There will obviously be a reduction in
12
13 the total volume, and the fractional change is given by:
14

$$\frac{\Delta V}{V} = \frac{-x_A v_A^0}{x_A v_A^0 + x_B v_B^0} \quad (19)$$

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21 which is obtained by simply dividing top and bottom by the total mass.
22

23
24 This means that the *ideal variation* in flow rate from the adsorption column would be:
25

$$r = 1 \quad (t < 0) \quad r = 1 - \frac{x_A v_A^0}{x_A v_A^0 + x_B v_B^0} \quad (0 < t < t_{\text{retn}}) \quad r = 1 \quad (t > t_{\text{retn}}) \quad (20)$$

26
27
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31 where t_{retn} is the retention time for the (sharp) composition front. Assuming that the specific
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33 volumes of the two liquids are comparable, for $x_A = 0.01$ there will be approximately a 1%
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35 reduction in the volumetric flow rate leaving the column as the composition front passes
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37 through the column. In order to obtain this “ideal” profile, we have assumed the
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39 concentration profile is a sharp front (instantaneous equilibrium and no axial dispersion) and
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41 that component A is strongly adsorbed (all of component A passes into the adsorbed phase).
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45 This ideal profile has limitations, but it does provide a useful comparison for the modelling.
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48 **Modelling of variation of column outlet flow rate with time**

49 ***Influence of shape of concentration front***

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52 From the previous section, the column outlet flow rate ($Q(t)$) will start at the baseline value
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54 ($Q(0)$), then reduce to the plateau value (Q_{plat}) as the concentration front passes through the
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56 column, and finally return to the baseline value. The variation in the outlet concentration
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4 $(c(t))$, however, will have a *different* shape: “nothing” will be apparent until the concentration
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6 front leaves the column, in which case there will be a “sweep” or sharp transition to the
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8 concentration of component A in the feed. In this section, the objective is to model the actual
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10 variation in $Q(t)$ for a variety of concentration front shapes or variation.
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12
13 For a *single* adsorbable component, the material balance (Seidel-Morgenstern, 2004) is
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15 written as
16

$$17 \frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q(c)}{\partial t} + u \frac{\partial c}{\partial z} = D_L \frac{\partial^2 c}{\partial z^2} \quad (21)$$

18
19 where u is the linear velocity, ε is the voidage in the column and z is the axial position along
20
21 the column. The parameter q is the adsorbed-phase concentration of component A. The
22
23 implication of the term (c) next to q allows the equilibrium adsorbed-phase concentration to
24
25 be used: that is, the isotherm. The advantage of this approach is that the contributions to band
26
27 broadening (axial dispersion and slow mass transfer processes) are all contained within a
28
29 single *apparent* dispersion parameter (D_L). For the sake of convenience, the adsorption
30
31 equilibrium is represented by the Langmuir isotherm
32
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34
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38

$$39 q = \frac{ac}{1+bc} \quad (22)$$

40
41 where a can be considered a type of Henry coefficient and b is the Langmuir parameter. As c
42
43 tends to zero, the isotherm becomes linear. The isotherm gradient is given by
44
45
46
47

$$48 \frac{dq}{dc} = \frac{a}{(1+bc)^2} \quad (23)$$

49
50 As the value of c tends to zero, the isotherm tends to a linear form with a equivalent to the
51
52 Henry constant. Here, we consider the section of isotherm to be *linear* with gradient equal to
53
54 a . Equation (21) can be solved with the relevant boundary conditions: for an adsorption
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56 experiment, initially the column is completely free of the adsorbed component (A), and then
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4 at $t = 0$, the concentration of component A undergoes a step change to c_0 . The solution is then
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6 given by $[c(z,t); q(z,t)]$ which shows how the concentration of component A varies with time
7
8 at any location (axial position z) in the column. For a composition detector, located at the end
9
10 of the column, the response is given by $c(L,t)$, where L is the length of the column.

11 12 ***Simplified solution of material balance***

13
14
15 We now return to the variation of the outlet flow rate from the column. In the previous
16
17 section, an expression was given for r assuming that component A is very strongly adsorbed:
18
19 equivalent to assuming that the value of the parameter a in Equation (22) is very large. In
20
21 reality, we take account of the isotherm gradient and column voidage, and so the parameter r
22
23 will depend on the fraction of the adsorbed component that enters the adsorbed phase:
24
25
26

$$27$$

$$28 \quad r = 1 \quad (t < 0) \quad r = 1 - \left[\frac{(1 - \varepsilon)a}{\varepsilon + (1 - \varepsilon)a} \right] \frac{x_A v_A^0}{x_A v_A^0 + x_B v_B^0} \quad (0 < t < t_{\text{retn}}) \quad r = 1 \quad (t > t_{\text{retn}}) \quad (24)$$

$$29$$

$$30$$

$$31$$

32
33 It is convenient to plot the profiles in terms of a *dimensionless time* (t^*), which is defined by
34
35 the time divided by the simple residence time (t_{void}). Figure 3 shows the idealised variations
36
37 in the column outlet flow rate for a mole/mass fraction (x_A) of 0.06 and a voidage (ε) of 0.75.
38
39 The two series correspond to different isotherm gradients: $a = 3$ and $a = 6$.
40
41

42 43 ***Equilibrium-dispersion model***

44
45 From Equation (8), the amount adsorbed (value of q) depends only on the area enclosed by the
46
47 variation in flow rate, and is independent of any band-broadening effects. This means that if
48
49 axial dispersion (a finite value of D_L) is imposed on one of the profiles in Figure 3, the
50
51 resulting profile will simply have a *broader* front as the concentration front leaves the column
52
53 – but, the area formed by the variation $Q(t)$ bound by a horizontal line at $Q(0)$ will remain
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55 *constant* and independent of the value of D_L .
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Equation (21) can be solved to give an analytical solution (Levenspiel and Bischoff, 1963). This is shown modified so that the dimensionless time is based on the simple residence time in the column. Furthermore, this is the asymptotic form and assumes instantaneous equilibrium and a long column.

$$\frac{c}{c_0} = \frac{1}{2} \operatorname{erfc} \left[\frac{1 - \frac{t}{t_{\text{void}}} \frac{\varepsilon}{\varepsilon + (1 - \varepsilon)a}}{2 \left(N_D \frac{t}{t_{\text{void}}} \frac{\varepsilon}{\varepsilon + (1 - \varepsilon)a} \right)^{0.5}} \right] \quad (25)$$

where N_D is the dispersion number which is equal to (D_L/uz) .

Figure 4 shows the variation in the column outlet flow rate for two values of the dispersion number: 0.01 for the solid line and 0.05 for the dotted line. This should be compared with the solid line of Figure 3, which corresponds to a zero dispersion number. In each of the cases shown in Figures 3 and 4, the concentration front entering the column is sharp; then, the effects of axial dispersion will cause the width of the concentration front to increase as it travels through the column.

Experimental arrangement

From the previous section, adsorption from the liquid phase will cause a *reduction* in the outlet flow rate from the column, and that this reduction is related to a number of factors. This means that there are two important implications for the design of an experimental arrangement to measure adsorption from the liquid phase.

1. A requirement of the material balance is that the flow rate of the feed ($Q(t)$) should be maintained as constant as possible. This will ultimately determine the range of applications of the method. For example, it will be impossible to monitor adsorption from the liquid phase where component A is present at a concentration of 100 ppm if the flow rate of the feed can only be maintained to $\pm 5\%$.

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4 2. We also require a sensitive method of *measuring* these small changes in flow rate. We
5
6 have alluded to this previously by considering that the variation in the volumetric flow rate
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8 leaving the column can be inferred from the pressure drop across a length of resistance tubing.
9

10
11 The experimental arrangement is intended *only* to simulate the *change* in the outlet flow from
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13 the baseline value of $Q(0)$ to the plateau value of Q_{plat} . This will then be compared to the
14
15 baseline variation in the value of $Q(0)$ (which we hope will remain as constant as possible),
16
17 from which an assessment of the sensitivity of the arrangement can be inferred.
18

19
20 For this purpose we have used the gravity-driven system shown in Figure 5. There are two
21
22 ways of ensuring that the flow rate remains constant in a gravity-driven system. First, we
23
24 could employ a very large tank with a large cross-section and a large resistance to give a low
25
26 flow rate so that the liquid level remains essentially constant during the experiment.
27
28 However, there may be problems with evaporation from the liquid surface, especially for a
29
30 volatile mobile phase. The alternative is to employ a weir system, where a flow rate of liquid
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32 higher than the system flow is directed into a beaker, and the excess flows over the side of the
33
34 container or through a weir. We adopted the latter approach for this investigation.
35
36
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39
40 The area surrounded by the dashed line is intended to represent the variation in column outlet
41
42 flow rate that occurs in a liquid adsorption system when the concentration front is travelling
43
44 through the column. Initially, valve V1 is open and valve V2 is closed and this represents the
45
46 baseline state of the system. Then valve V2 is open to increase the flow rate through the
47
48 measuring resistance (k_C). This would then represent what might happen during a desorption
49
50 experiment, where the adsorbed component leaves the adsorbed phase and passes into the
51
52 liquid phase. For example, in Figure 3 this would correspond to the change in outlet flow rate
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54 from the plateau value (Q_{plat}) to the baseline value ($Q(0)$).
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58
59 Because we only had a fixed amount of ethanol, it was necessary to recycle the flows back to
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61 the tank. The weir was simply a large hole in the side of the beaker with a large-diameter
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4 length of tubing to direct the flow to the return beaker. The liquid level in the supply beaker
5
6 was approximately 30 cm above the bench surface. The “baseline” ethanol flow rate was
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8 determined by the flow resistances k_A and k_C . These are different lengths of stainless-steel
9
10 tubing with an internal diameter of about 1 mm. The length of resistance k_A was about 50 cm
11
12 and the length of resistance k_C was about 3 cm meaning that the ratio of k_A to k_C was close to
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14 20. Resistance k_B had a length of about 20 cm but a much smaller bore (about 0.5 mm),
15
16 meaning that the value of k_B was perhaps an order of magnitude greater than k_A . The two
17
18 shut-off valves (V1 and V2) were Whitey ball-valves. The volumetric flow rate of ethanol
19
20 was measured by directing the flow from resistance C into a measuring cylinder.
21
22

23
24 It could be argued that since this is a closed system, there should be no need to have the weir,
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26 since the liquid level in the tank *should* be constant. However, in a preliminary experimental
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28 arrangement without the weir, close inspection of the liquid level in the tank indicated that the
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30 liquid level might fluctuate in a typical hour time-scale by about 1 mm. This corresponds to a
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32 change in pressure head of 0.1 mbar. The reasons for this may be evaporation of ethanol and
33
34 any slight changes in the rate at which liquid is pumped back into the supply beaker and the
35
36 time for which the ethanol flow rate is measured by directing the flow away from the return
37
38 beaker. The pressure drop across resistance k_c was measured with a Validyne 55 pressure
39
40 transmitter with a ± 14 mbar range corresponding to an output of ± 5000 mV. The signal
41
42 voltage was measured every 1 second and recorded using a Pico data acquisition system.
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47

48 **Experimental procedure and recorded pressure transmitter data**

49

50
51 1. The first stage was to prime the equipment. This was achieved by opening the two shut-
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53 off valves (V1 and V2) and switching on the pump, allowing the ethanol to flow through the
54
55 whole system. Then valve V2 was closed and for the first experiment, the baseline value of
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57 $P_2(t)$ was monitored for 400 seconds. This was essential, as the likely applications (or
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59 limitations) of this equipment are likely to be determined by how constant we can maintain
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4 the baseline voltage and the main flow rate. This is shown in Figure 6. It can be seen that the
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6 signal drifts up by 0.3 mV (0.00084 mbar) in the first 200 seconds, and then down by 0.2 mV
7
8 (0.00056 mbar) in the remaining 200 seconds. The baseline flow rate has a value Q_1 .
9

10
11 2. For the second experiment, valve V2 was opened to allow ethanol to flow through
12
13 resistance k_B and so increase the ethanol flow rate through the measuring resistance to a value
14
15 Q_2 . The valve was opened at a time of around 440 seconds. It can be seen that there is a
16
17 steady increase in P_2 , from 184.57 mV to 202.06 mV: a change of 17.49 mV (0.049 mbar).
18
19 The new steady-state took about 100 seconds to be achieved. Then, valve V2 was closed to
20
21 stop ethanol flowing through resistance k_B and into the supply beaker. The valve was closed
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23 at a time of around 620 seconds. As expected, this leads to a reduction in the value of P_2 from
24
25 202.02 mV to 184.46 mV: a change of 17.56 mV (0.049 mbar). The complete pressure record
26
27 for P_2 is shown in Figure 7, and it can be seen that there is a net drift by only 0.11 mV (0.0003
28
29 mbar), which is encouraging considering the experimental time.
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34 **Calculation of equipment sensitivity for potential adsorption experiments**

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37 For a favourable experimental design we require that the drifting should be as *low* as possible
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39 in Figure 6 and that the step-change in Figure 7 should be as *large* as possible. Consider the
40
41 step-change experiment in which the initial flow rate is Q_1 and the final flow rate is Q_2 . It is
42
43 appropriate to be able to quantify how well the experimental arrangement might perform for
44
45 adsorption experiments and for convenience the parameter of performance (α) is defined by
46
47
48

$$49 \alpha = \frac{[\Delta P_2] \text{ (drift) (mV)}}{[\Delta P_2] \text{ (step) (mV)}} \times \left[\frac{Q_2}{Q_1} - 1 \right] \quad (26)$$

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53

54 Note that for a successful experimental arrangement, the value of α should be as *small* as
55
56 possible. Let us consider a notional example. Consider that the drift over a particular time
57
58 spell is 0.01 mV, and that the step change is 100 mV for a fractional increase in flow rate of
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4 1%. This would give a value of 10^{-6} which would be very favourable, since it would be
5
6 capable of measuring tiny flow rate changes corresponding to systems where the adsorbate is
7
8 present at low concentrations. As we shall see, the actual value of α for the current
9
10 experimental arrangement is not as favourable. We now proceed to obtain an expression for α
11
12 in terms of the various experimental parameters.
13
14

15
16 The first stage is to identify and quantify the possible sources of drifting in the baseline shown
17
18 in Figure 6. Assuming laminar flow through both resistances k_D and k_F , we can write
19
20

$$21 \quad P_2 - P_3 = \frac{k_F \mu_F}{k_D \mu_D + k_F \mu_F} \rho g h \quad (27)$$

22
23
24
25 From Equation (27), we can identify three possible reasons to explain why the variation
26
27 shown in Figure 6 is not a horizontal line. First, there may be variation in the level of ethanol
28
29 in the tank. The weir is designed to maintain this level constant, but this may not be perfect.
30
31 Second, there may be changes in the overall liquid temperature which will change the density.
32
33 Third, over the course of the experiment, the temperatures in the two resistances may change
34
35 by different amounts. Consider that the ethanol in resistance k_F changes by 0.1°C but the
36
37 ethanol in resistance k_D stays at the same value. This effect is included because the liquid
38
39 viscosity is a strong function of temperature (Yaws, 1999). From differentiation, these three
40
41 sources of drifting (level, density and viscosity) are quantified as
42
43
44
45

$$46 \quad \Delta P_2(h) = \frac{\mu_F k_F}{\mu_D k_D + \mu_F k_F} \rho g \Delta h \quad (28)$$

$$47 \quad \Delta P_2(\rho) = \frac{\mu_F k_F}{\mu_D k_D + \mu_F k_F} g h \Delta \rho \quad (29)$$

$$48 \quad \Delta P_2(T) = \frac{k_D k_F}{(k_D \mu_D + k_F \mu_F)^2} (\mu_D \Delta \mu_F - \mu_F \Delta \mu_D) \rho g h \quad (30)$$

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4 The value of the drift term in Equation (26) is then simply the sum of these three terms. The
5
6 next stage is to simplify the term in Equation (26) involving the ratio of Q_2 to Q_1 . The
7
8 “before” state of the system (before valve V2 is open) can be written as
9

$$10 \quad P_2 - P_3 = k_F \mu_F Q_1 \quad (31)$$

$$11 \quad P_1 - P_3 = (\mu_D k_D + \mu_F k_F) Q_1 \quad (32)$$

12
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14
15
16 and the “after” state can be written as

$$17 \quad (P_2 + \Delta P_2(\text{step})) - P_3 = k_F \mu_F Q_2 \quad (33)$$

$$18 \quad P_1 - P_3 = \mu_D k_D (Q_2 - Q_3) + \mu_F k_F Q_2 \quad (34)$$

19
20 Equations (31) to (34) can be solved to eliminate Q_3 and give an expression for the ratio of the
21
22 “initial” and “final” ethanol flow rates. This can be simplified by assuming that the values of
23
24 μ_A and μ_B are the same:
25
26

$$27 \quad \frac{Q_2}{Q_1} = 1 + \frac{k_D}{k_F} \left[1 + \frac{k_E}{k_F} + \frac{k_E}{k_D} \right]^{-1} \quad (35)$$

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39 Our measurements indicate that opening the valve V2 increases the volumetric flow rate by
40
41 about 15%. We know that the ratio of k_D to k_F is approximately 20 and so from Equation (35)
42
43 the ratio of k_E to k_D is about 6. This is in accordance with our expectations: the resistance of a
44
45 length of tubing is inversely proportional to the internal diameter to the fourth power (Coulson
46
47 and Richardson, 1999). The form of Equation (35) can be checked by intuition. As the value
48
49 of k_E is increased, the ratio of the two flow rates tends to unity: opening the valve V2 will
50
51 have zero effect on the flow rate through resistance F.
52
53

54
55 We return to the final term in Equation (26). Subtracting Equation (31) from (33) we obtain:
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57

$$58 \quad \Delta P_2(\text{step}) = k_F \mu_F (Q_2 - Q_1) \quad (36)$$

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4 and then using Equation (35) we have the useful form
5
6

$$\Delta P_2(\text{step}) = \rho g h \frac{k_D}{k_D + k_F} \left[1 + \frac{k_E}{k_F} + \frac{k_E}{k_D} \right]^{-1} \quad (37)$$

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11 Once again, Equation (37) can be checked to confirm what we expect from intuition: a zero
12 value of k_F will give an expected zero step-change in ΔP_2 . Furthermore, an infinite value of k_E
13 will make zero difference to the flow rate and an expected zero step-change of ΔP_2 . Finally,
14 we can combine Equations (28) to (30), (35) and (37) to obtain:
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$$\alpha = \frac{\Delta h}{h} + \frac{\Delta \rho}{\rho} + \frac{k_D}{k_D + k_F} \left[\frac{\Delta \mu_F - \Delta \mu_D}{\mu} \right] \quad (38)$$

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22
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26 This is interesting for a number of reasons. Note that the resistance k_E does *not* appear in the
27 above equation. This is what would be expected: the resistance k_E is only used to change the
28 system flow. If we assume that variation in the level of liquid (h) is the main reason for the
29 baseline drift, then the value of α is *independent* of the values of the two flow resistances.
30 This is because as the values of k_D and k_F are changed, both the drift and step-change values
31 of ΔP_2 in Equation (26) change by the same amount. If, however, we assume that the main
32 source of baseline drift is the temperature changing by different amounts in the two
33 resistances (so that the values of $\Delta \mu_D$ and $\Delta \mu_F$ are not the same), then this can be reduced by
34 reducing the value of the main-flow resistance (k_D).
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47 We can now calculate the actual value of α for the experiments shown in Figures 6 and 7.
48 From Figure 6, the average drift in baseline over a 100-second timescale is about 0.1 mV.
49 From Figure 7, an increase of the flow through the measuring resistance of 15% corresponds
50 to a step change in the signal of about 20 mV. These parameters show that
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$$\alpha = \frac{0.1}{20} \times (1.15 - 1) = 0.00075$$

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4 This is the order of 10^{-4} of the original flow rate. If we assume a resolution of one part in 100,
5
6 this would mean that we could use the current experimental arrangement to measure the
7
8 adsorption of solutes present at levels of the order of 10^{-2} . A typical example might be an
9
10 investigation of a new adsorbent to dry an ethanol stream containing 5% of water. The natural
11
12 question is then how we might improve the arrangement to measure the adsorption of solutes
13
14 present at much lower concentration levels – say an order of magnitude reduction to 1000
15
16 ppm, since this would open up a large number of new applications.
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18
19

20 Discussion

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23 1. We first of all consider whether it is possible to determine the source of the baseline
24
25 drifting in Figure 6. This will be achieved by predicting α according to Equation (38). The
26
27 obvious reason might be that the liquid level (h) in the tank will vary with time. Observation
28
29 would suggest that the liquid level might be maintained to perhaps 0.5 mm for which
30
31

$$32 \alpha = \frac{\Delta h}{h} = \frac{0.5}{300} = 0.0017$$

33
34 This is about twice the actual value (0.00075), and so would suggest that h might be
35
36 maintained to around 0.25 mm: the liquid level may indeed be the major reason for the drift in
37
38 the baseline. The second term in Equation (38) concerns drifting due to the change in density.
39
40 The densities of ethanol at 21.0°C and 21.1°C are 791.4 kg/m³ and 791.3 kg/m³ respectively.
41
42 Therefore, if the temperature of the entire liquid column varies by 0.1°C, then we can write
43
44
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$$48 \alpha = \frac{\Delta \rho}{\rho} = \frac{0.1}{790} = 0.00013$$

49
50 This is a factor of six smaller than the actual value (0.00075), and would suggest that this is
51
52 not a likely reason for the baseline drift. We finally consider that the temperature in the two
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54 resistances might not be the same. The viscosity of a liquid is very sensitive to temperature:
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4 for ethanol, the viscosities at 20.0°C and 20.1°C are 1.145 and 1.143 cP respectively.
5
6 Consider that the temperature of ethanol in resistance k_F increases by 0.1°C and that the
7
8 temperature of resistance A remains the *same*. We can then write
9

$$\alpha = \frac{k_D}{k_D + k_F} \left[\frac{\Delta\mu_F - \Delta\mu_D}{\mu} \right] = \frac{20}{20 + 1} \left[\frac{0.002}{1.145} \right] = 0.0017$$

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15 This is significant, and would indicate that insulation of the experimental arrangement from
16
17 changes in ambient temperature is more important than we had considered at the outset. At
18
19 present, the whole arrangement is simply placed on the top of a bench.
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23 From the three calculations, there may be two ways in which the experimental arrangement
24
25 could be improved to reduce the level of drifting. First, to increase the value of h by say a
26
27 factor of 10 and place the liquid beaker close to the roof of the laboratory. Second, to increase
28
29 the value of k_F relative to the value of k_D . The current values are 20 and 1, respectively; an
30
31 improvement would be to change these values to 14 and 7 so that the sum remains constant.
32
33
34 These changes might reduce the drifting by a factor of 10.
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36

37 2. There is another quite different reason why the baseline might vary with time. The
38
39 liquid is likely to contain particles that originate from the equipment, and the associated
40
41 wetted surfaces. As these particles are carried around the system, they may cause temporary
42
43 blockages in the capillary tubes. Furthermore, according to the classical theory of Einstein,
44
45 the presence of particles as a suspension will cause a slight increase in the viscosity (μ). This
46
47 may vary with time as the particles settle and pass into the flowing liquid.
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49
50

51 3. There are a number of ways in which the experimental arrangement might be improved.
52
53 The flow resistances are various length of stainless-steel tubing with an internal diameter of
54
55 either 0.5 mm or 1 mm. The same values of resistance might be achieved by using nylon
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57 tubing with *larger* inside diameters and *longer* lengths. The larger diameter might be less
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4 susceptible to any entrained particles in the ethanol. Another possible modification concerns
5
6 the supply beaker: the same beaker is used for both liquid flows. It is possible that when the
7
8 valve V2 is opened to allow the flow through resistance k_E , this might cause a sudden (but
9
10 tiny) drop in the liquid level causing a slight reduction in the flow through resistance k_D . This
11
12 could be avoided by an extra supply beaker for the flow through resistance k_E .
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14

15
16 4. There are two potential problems regarding the transfer of heat between the liquid
17
18 flowing through the capillary tubes and the surroundings. First, as discussed in Point 1, there
19
20 is the potential for local changes in ambient temperature to change the liquid viscosity in each
21
22 resistance by different amounts. To this end, we would require the overall heat-transfer
23
24 coefficient (U) to be as low as possible. However, adsorption in the liquid phase can be a
25
26 fairly exothermic process (where the temperature change can exceed 10°C). To that end, we
27
28 would require the “heated” liquid mixture leaving the adsorption column to “lose” this excess
29
30 heat as quickly as possible: major requirements are that the viscosity of liquid in the
31
32 measurement resistance (k_F) should remain constant and that the whole system return to
33
34 ambient temperature before completion of the experiment. To this end, we would require that
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36 U should be as high as possible.
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42 The flow through the tubing is laminar for which heat is transferred from the inside of the tube
43
44 to the liquid by conduction. This is a special case for which the Nusselt number = 3.66
45
46 (constant wall temperature). This allows determination of the heat-transfer coefficient (h_{con}):
47
48

$$49 \quad Nu = \frac{h_{con}d}{k} \rightarrow h_{con} = \frac{3.66 \times 0.2}{0.001} = 732 \text{ (W/m}^2\text{K)}$$

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52

53
54 for a tube with an inside diameter of 1 mm (ethanol has a k value of 0.2 W/mK). Depending
55
56 on the mode of heat transfer between the surroundings and the tube wall, the value of U might
57
58 vary from 10 to 500 W/m²K. This might suggest that the best choice would be to place the
59
60 capillaries and associated tubing in a constant-temperature enclosure with a high value of U .
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4 5. A good choice for a first experimental investigation would be the water–ethanol system.
5
6 Lau et al. (2004) used a column of length 47 cm and diameter 5 cm packed with spherical
7
8 beads of 3A zeolite. The intention was to dry a mixture containing about 3% by weight of
9
10 water. A flow rate of 16.5 mL/min was set and the column outlet analysed to obtain the
11
12 breakthrough curve ($c(L,t)$). This started at a time of about three hours and was complete by
13
14 about seven hours. Adsorption of water onto zeolite is an exothermic process, and the
15
16 concentration front was accompanied by a thermal wave with a peak temperature 20°C greater
17
18 than the ambient temperature. According to the equilibrium loading data, the water is
19
20 strongly adsorbed, with the value of a greater than 5. A better choice of operating conditions
21
22 might be to reduce the column volume by a factor of 100, the diameter by a factor of 5 and the
23
24 flow rate by a factor of 10. This would allow the experimental time to be reduced by a factor
25
26 of 10, and suppress the formation of any thermal wave through the column. Furthermore, a
27
28 major advantage of monitoring the flow rate is that a key parameter is the fractional reduction
29
30 in column outlet flow rate that occurs *straightaway* when the concentration front enters the
31
32 column. This fractional reduction is independent of the amount of packing, although it will
33
34 depend on the voidage in the column.
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41 6. We now return to the component material balance shown in Equation (12). This can be
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43 written in a more-convenient form and then integrated to give:
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$$45$$

$$46$$

$$47 (\Delta m_A)_{\text{ads}} + (\Delta m_A)_{\text{liq}} = Q(0) \int_0^{\infty} [c_0 - c(t)] dt + \int_0^{\infty} c(t) [Q(0) - Q(t)] dt \quad (39)$$

$$48$$

$$49$$

50
51 The first integral term is the “standard” term for breakthrough of the concentration front. The
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53 second integral term is a correction to allow for the variation in the outlet flow rate with time.
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55 The function within the integral will take the form of a peak since it will be zero at time zero,
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57 and then zero after breakthrough of the concentration front is complete. For a “vertical” or
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59 “sharp” concentration front, the integral will have a zero value. Indeed, the value of the
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4 integral will *increase* with the width of the concentration front. This has important
5
6 implications. Since the area given by Equation (8) is fixed for a particular value of $(\Delta m)_{\text{ads}}$,
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8 then the individual integrals in Equation (39) will vary with the width of the concentration
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10 front.

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13 7. In Equations (18) and (19), it was assumed that the liquid mixture is ideal. In reality,
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15 Equation (19) should be re-written as

$$\frac{\Delta V}{V} = \frac{x_B(v_A^0 - v_B) - x_A v_A}{x_A v_A + x_B v_B} \quad (40)$$

16
17
18 where v_A and v_B are the partial specific volumes of components A and B, which vary with
19
20 composition of the liquid mixture. Typically, the difference between using Equation (19) and
21
22 (40) might be of the order of a few %.

23 24 25 26 27 28 29 30 31 **Conclusions**

32
33 For the measurement of adsorption of a single component from the liquid phase, the standard
34
35 approach is to monitor the concentration of the adsorbed component in the outlet flow from
36
37 the adsorption column. In this work, we consider how adsorption might be measured by
38
39 monitoring the variation in the *actual* outlet flow rate. One advantage of this approach is that
40
41 there will be a step-reduction in the outlet flow rate that occurs as *soon* as the concentration
42
43 front enters the column; moreover, from the material balance this reduction will stay at a
44
45 constant level before the start of breakthrough. This is preferable to the “concentration”
46
47 approach, where it is necessary to wait until breakthrough of the front is complete, which can
48
49 take a number of hours. A major requirement of the developed theory is that the flow rate of
50
51 the feed to the adsorption column should be maintained as *constant* as possible: this then
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53 determines the sensitivity of the equipment. Our results would suggest that a gravity-driven
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55 system with a liquid head of 30 cm is capable of monitoring a strongly-adsorbed component
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4 present in the liquid phase at a mass fraction of about 1%. The limiting factor is how constant
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6 the liquid level in the feed tank can be maintained. Increasing this height by a factor of 10
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8 should allow the method to deal with a component present at a level of about 1000 ppm. An
9
10 alternative for future investigations might be to replace the gravity-driven system with a series
11
12 of syringe or piston pumps.
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14

15 **Acknowledgement**

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19 This work was supported by the Engineering and Physical Sciences Research Council
20
21 (EPSRC) and the Nuffield Foundation (NAL/00624/G).
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23

24 **Nomenclature**

25	
26	
27	a Gradient of isotherm
28	
29	$c(L,t)$ Concentration of component A in flow leaving column (g/L)
30	
31	
32	c_0 Concentration of component A in feed to column (g/L)
33	
34	D_L Effective axial dispersion coefficient in column (m^2/s)
35	
36	h Liquid head (cm)
37	
38	h_{con} Heat-transfer coefficient between inside tube wall and ethanol flow ($\text{W}/\text{m}^2\text{K}$)
39	
40	
41	k_D Flow resistance to set initial flow (m^{-3})
42	
43	
44	k_E Flow resistance to add extra ethanol flow (m^{-3})
45	
46	k_F Flow resistance to measure total ethanol flow leaving system (m^{-3})
47	
48	
49	L Length of column (cm)
50	
51	$(m_A)_{\text{ads}}$ Mass of component A in adsorbed phase in the column (g)
52	
53	$(m_A)_{\text{liq}}$ Mass of component A in liquid phase in the column (g)
54	
55	$(m_B)_{\text{liq}}$ Mass of component B in liquid phase in the column (g)
56	
57	N_D Dispersion number
58	
59	
60	P_1 Atmospheric pressure (Pa or bar)
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4	P_2	Pressure used to monitor flow rate leaving system (Pa or bar)
5		
6	P_3	System discharge pressure (Pa or bar)
7		
8	q	Concentration of adsorbed component in adsorbed phase (g/L)
9		
10	$Q(t)$	Volumetric flow rate leaving column at time t (mL/min)
11		
12	Q_{plat}	Constant-value value of $Q(t)$ before start of breakthrough (mL/min)
13		
14	Q_1	Volumetric flow of ethanol in initial state (with V1 only open) (mL/min)
15		
16	Q_2	Volumetric flow of ethanol after opening valve V2 (mL/min)
17		
18	Q_3	Volumetric flow of ethanol through resistance B when valve V2 is open (mL/min)
19		
20	r	Ratio of actual flow rate to initial flow rate leaving column
21		
22	t_{retn}	Time taken for (sharp) concentration front to emerge from column (s)
23		
24	t_{void}	Simple residence time in column (s)
25		
26	u	Fluid-phase velocity in adsorption column (m/s)
27		
28	U	Overall heat-transfer coefficient (U) between ambient and ethanol ($\text{W}/\text{m}^2\text{K}$)
29		
30	v_A^0	Specific volume of component A at the system pressure and temperature (mL/g)
31		
32	v_B^0	Specific volume of component B at the system pressure and temperature (mL/g)
33		
34	V	Volume of liquid (mL)
35		
36	W	Mass of adsorbent (g)
37		
38	x_A	Mass fraction of adsorbed component (A)
39		
40	x_B	Mass fraction of non-adsorbed component (B)
41		
42	z	Axial location in column (cm)
43		
44	α	Performance of experimental arrangement
45		
46	μ_B	Viscosity of non-adsorbed component B (kg/ms)
47		
48	μ_D	Viscosity of ethanol in resistance D (kg/ms)
49		
50	μ_E	Viscosity of ethanol in (flow-changing) resistance E (kg/ms)
51		
52	μ_F	Viscosity of ethanol in (flow-measurement) resistance F (kg/ms)
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4	ε	Column voidage
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6	$\rho(t)$	Density of outlet flow from column at time t (kg/m ³)
7		
8		
9	ρ_B	Density of non-adsorbed liquid B (kg/m ³)
10		
11	ρ_{feed}	Density of feed to adsorption column (kg/m ³)
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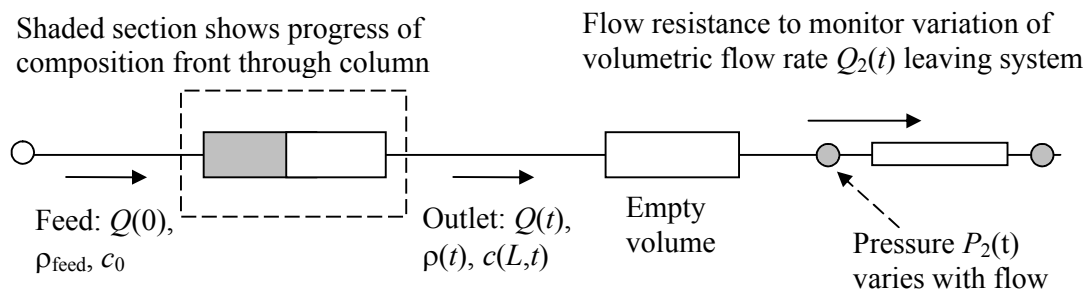


Figure 1: Schematic experimental arrangement for measuring adsorption in liquid systems. The empty volume is a key part of the experimental arrangement. It maintains a constant composition (component B) in the flow resistance while the composition front is travelling through the column.

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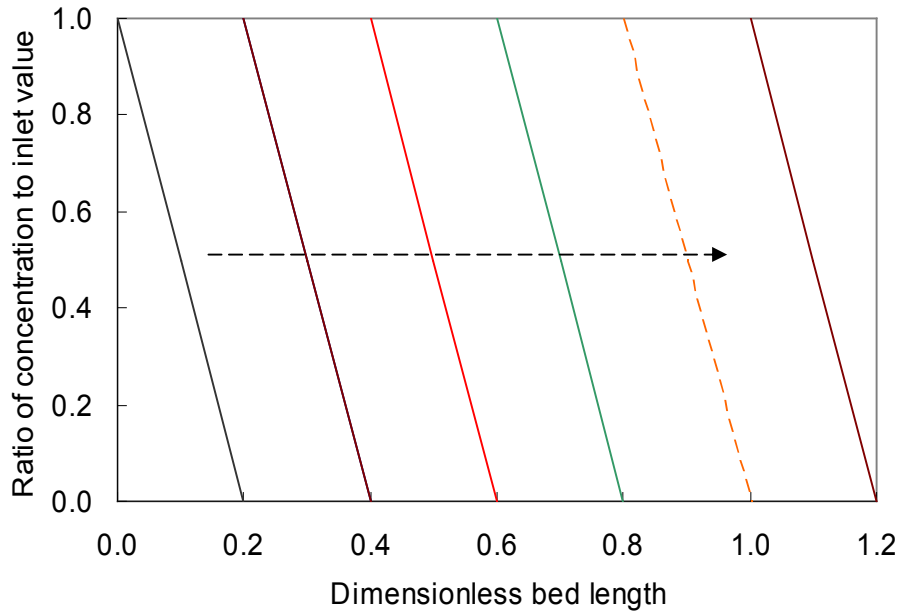


Figure 2: Passage of a concentration front of finite width through an adsorption column. The shape of the front remains constant because the dispersion effects are ignored. The arrow shows the progress of the front with time: the front shown with a dashed line corresponds to the start of breakthrough, and the final front corresponds to the completion of breakthrough.

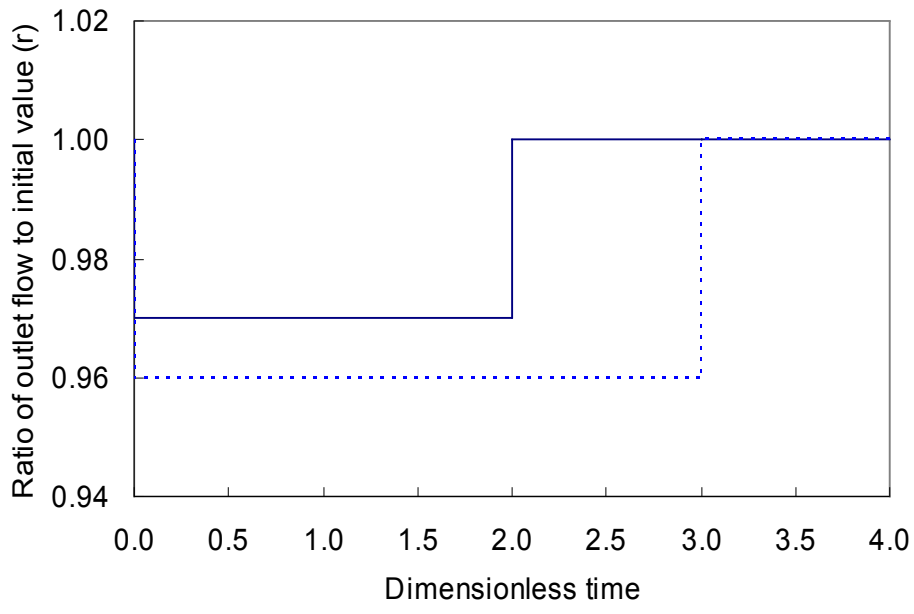


Figure 3: Idealised (linear isotherm, zero axial dispersion, instantaneous equilibrium) variation in the volumetric flow rate leaving the column. The dotted line corresponds to the more strongly-adsorbed component: $a = 6$ compared to $a = 3$. For each case, a sharp or vertical concentration front enters the column at time = 0.

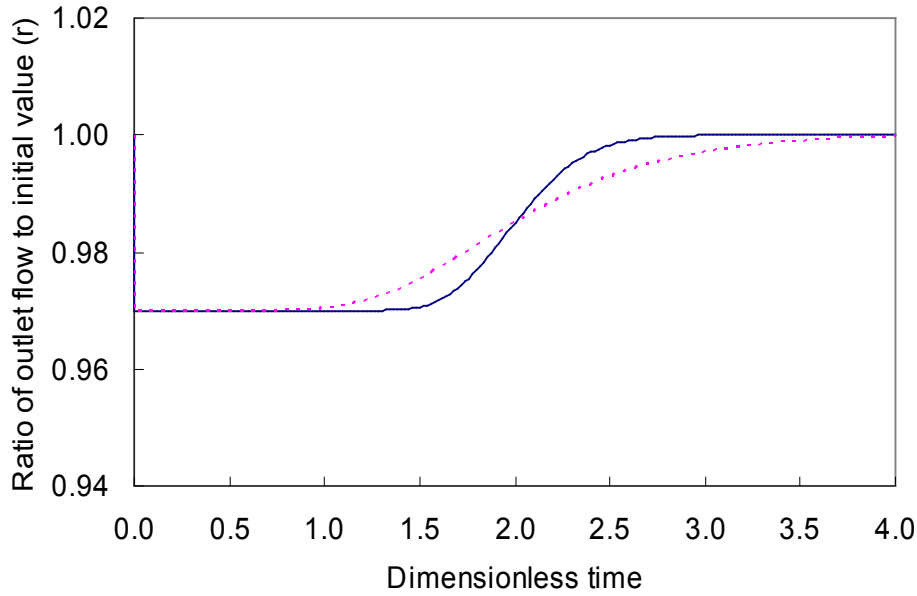


Figure 4: Actual variation in the column outlet flow rate for solution of the material balance with the inclusion of axial dispersion in the column. The solid line is for a dispersion number of 0.01 and the dotted line is for a dispersion number of 0.05.

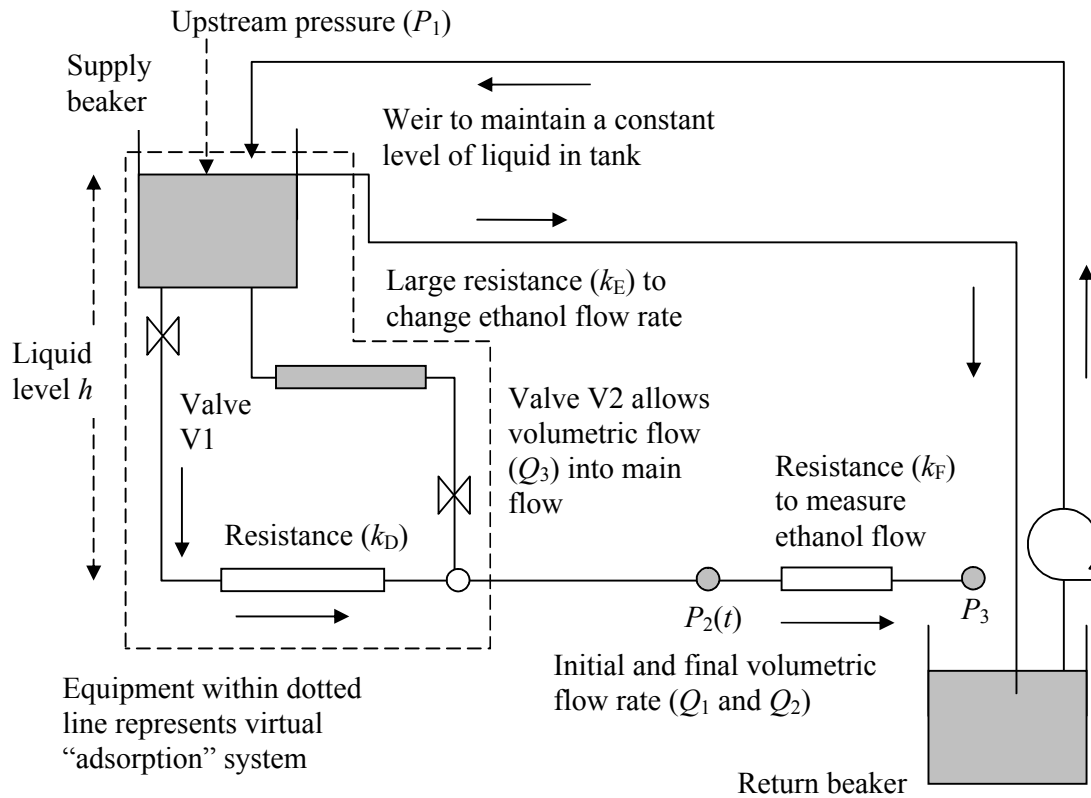


Figure 5: Schematic of actual experimental arrangement to assess the sensitivity of a gravity-fed system for the detection of changes in flow rate.

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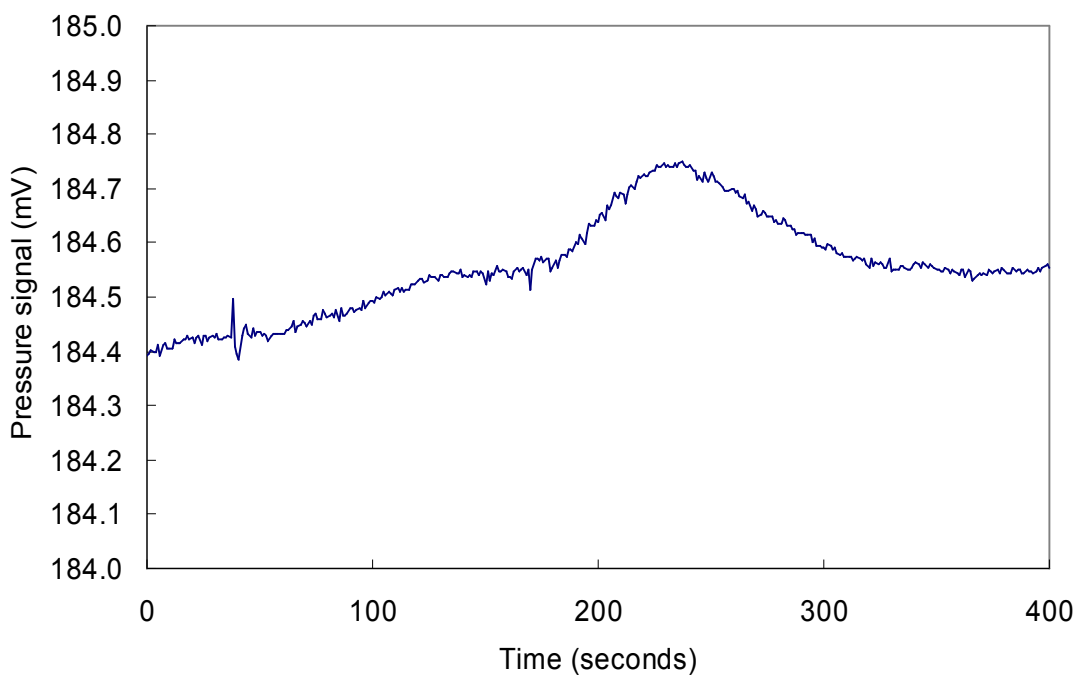


Figure 6: Baseline signal (variation in P_2) over 400 seconds, for which it can be seen that the voltage stays within a range of about 0.3 mV. The flow rate of ethanol through resistance C is about 1 mL/min. The 1 mV span corresponds to 0.0028 mbar.

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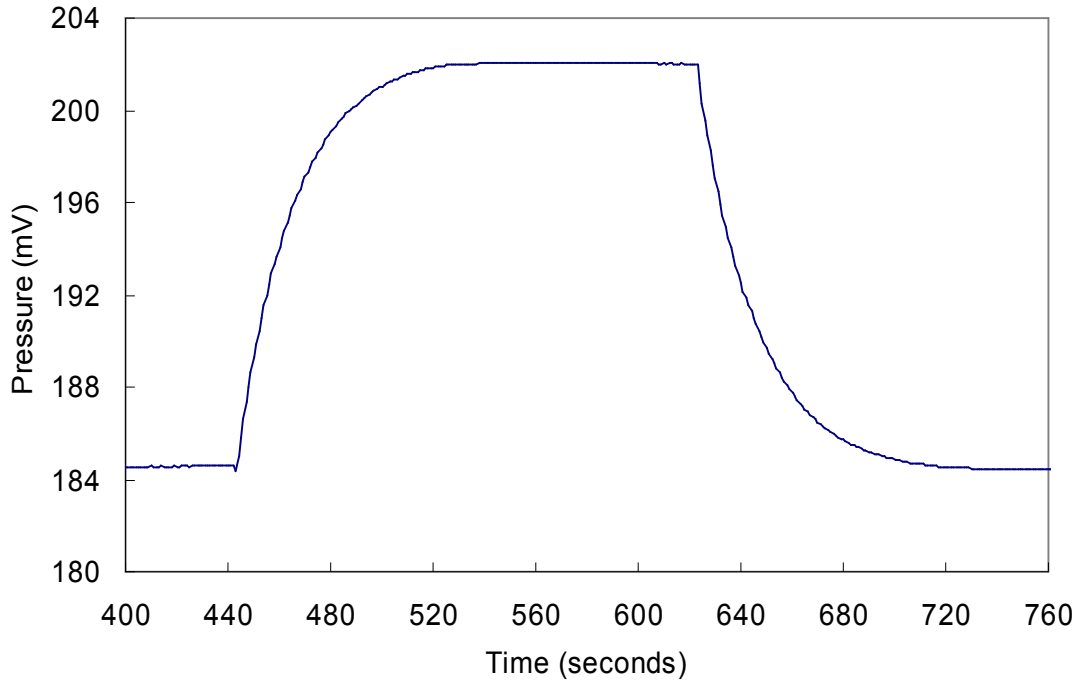


Figure 7: The first step in the pressure (P_2) signal is obtained by increasing the ethanol flow rate through the measurement resistance (k_C) by about 15%, from an original value of 1 mL/min. The second step is obtained by reducing the ethanol flow to the original value.