

Note

Measurement of variation of distribution coefficients for glucose and fructose with sugar concentration

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(Received August 2nd, 1985)

In a recent paper¹ Barker and Thawait reported information on the concentration dependence of the distribution coefficient (K) for aqueous solutions of fructose and glucose in ion-exchange resins, derived from measurements of retention volumes according to the expression:

$$V_R = V_m + KV_s \quad (1)$$

Eqn. 1 is actually a special case of the more general relationship:

$$V_R = V_m + V_s \cdot \frac{dq^*}{dc} \quad (2)$$

which, as shown in the Appendix, should be approximately valid for the systems in question. Clearly for a linear system $q^*/c \equiv K = dq^*/dc$ and eqn. 2 reduces to eqn. 1, which should therefore be always valid when the concentration of the species in question is small, regardless of the concentrations of the other components in the system. However, if the system is non-linear (K dependent on concentration) it is obviously incorrect to apply eqn. 1 at high sorbate concentrations since eqns. 1 and 2 are then no longer equivalent.

In the reported experiments retention volumes were measured for four different situations; a pulse of fructose injected into a carrier consisting of an aqueous solution of glucose or fructose and a pulse of glucose injected into a carrier containing either fructose or glucose. When the pulse is injected into a stream of the other component eqn. 1 is valid since the injected component is effectively at infinite dilution. However, when the pulse is injected into a carrier containing the injected component eqn. 1 is not valid and must be replaced by eqn. 2. Consequently the values given for the distribution coefficients in the latter cases should be re-interpreted as the derivatives and we have, from Table I of Barker and Thawait's paper¹:

$$\text{glucose in glucose: } \frac{dq_g^*}{dc_g} = 0.77 c_g + 0.1237$$

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$$\text{fructose in fructose: } \frac{dq_f^*}{dc_f} = 0.15 c_f + 0.386$$

By integration the expressions for the distribution coefficients are obtained as:

$$K_g \equiv \frac{q_g^*}{c_g} = 0.385 c_g + 0.1237$$

$$K_f \equiv \frac{q_f^*}{c_f} = 0.075 c_f + 0.386$$

Evidently the concentration dependence of the distribution coefficients for these cases is much less pronounced than the original interpretation of the data ($K_g = 0.77 c_g + 0.1237$; $K_f = 0.15 c_f + 0.386$) would suggest.

APPENDIX

The fundamental differential mass balance equation for an element of a chromatographic column with plug flow is:

$$v \cdot \frac{\partial c_i}{\partial z} + c_i \cdot \frac{\partial v}{\partial z} + \frac{\partial c_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q_i}{\partial t} = 0 \quad (\text{A1})$$

For a binary system such as glucose-water or fructose-water one has equations of this form for both components. Since the molecular weights and molar volumes of the two components are very different it is convenient to re-cast eqn. A1 in terms of mass fractions:

$$v \cdot \frac{\partial y_1}{\partial z} + y_1 \cdot \frac{\partial v}{\partial z} + \frac{\partial y_1}{\partial t} + \frac{q}{c} \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial x_1}{\partial t} = 0 \quad (\text{A2})$$

$$v \cdot \frac{\partial y_2}{\partial z} + y_2 \cdot \frac{\partial v}{\partial z} + \frac{\partial y_2}{\partial t} + \frac{q}{c} \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial x_2}{\partial t} = 0 \quad (\text{A3})$$

Multiplying eqn. A2 by y_2 and eqn. A3 by y_1 , subtracting, noting that $y_1 + y_2 = 1.0$ we obtain:

$$v \cdot \frac{\partial y_1}{\partial z} + \frac{\partial y_1}{\partial t} + \frac{q}{c} \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \left[(1 - y_1) \cdot \frac{\partial x_1}{\partial t} - y_1 \cdot \frac{\partial x_2}{\partial t} \right] = 0 \quad (\text{A4})$$

If we assume that on a mass basis there is no net flux into or out of the adsorbent, $\partial_1/\partial t = -\partial x_2/\partial t$ and eqn. A4 reduces to:

$$v \cdot \frac{\partial y_1}{\partial z} + \frac{\partial y_1}{\partial t} + \frac{q}{c} \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial x_1}{\partial t} = 0 \quad (\text{A5})$$

To calculate the velocity with which a concentration perturbation passes through the column we put:

$$\frac{\partial q_1}{\partial t} = q \cdot \frac{\partial x_1}{\partial t} = \frac{dq_1^*}{dc} \cdot \frac{\partial c_1}{\partial t} = c \cdot \frac{dq_1^*}{dc_1} \cdot \frac{\partial y_1}{\partial t} \quad (\text{A6})$$

thus reducing eqn. A5 to:

$$v \cdot \frac{\partial y_1}{\partial z} + \frac{\partial y_1}{\partial t} \left[1 + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{dq_1^*}{dc_1} \right] = 0 \quad (\text{A7})$$

Comparison with the standard first-order wave equation:

$$w \cdot \frac{\partial y}{\partial z} + \frac{\partial y}{\partial t} = 0 \quad (\text{A8})$$

shows that eqn. A7 represents a perturbation travelling with velocity:

$$w = \frac{v}{1 + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{dq_1^*}{dc_1}} \quad (\text{A9})$$

To translate this in terms of retention volumes we simply note that

$$\frac{V_R}{\text{total column volume}} = \frac{v}{w} \quad (\text{A10})$$

$$\begin{aligned} V_R &= \left[\varepsilon + (1 - \varepsilon) \cdot \frac{dq^*}{dc} \right] L \\ &= V_m + V_s \cdot \frac{dq^*}{dc} \end{aligned} \quad (\text{A11})$$

which is eqn. 2.

SYMBOLS

| | |
|-------|--|
| c | concentration of sorbate in aqueous phase |
| K | distribution coefficient (defined as q^*/c) |
| L | column length |
| q | concentration of sorbate in resin |
| t | time |
| v | interstitial fluid velocity |
| V_m | volume of fluid in column |
| V_R | retention volume |
| V_s | volume of solid adsorbent in column |

| | |
|---------------|---|
| w | velocity of concentration wave |
| x | mass fraction of sorbate in resin phase |
| y | mass fraction of sorbate in solution |
| z | distance measured along column |
| ε | voidage of adsorbent bed |

Subscripts 1, 2, i , g and f refer to species 1, 2, i , glucose and fructose, respectively.

Superscript * denotes equilibrium value.

REFERENCE

- 1 P. E. Barker and S. Thawait, *J. Chromatogr.*, 295 (1984) 479–485.