# A Study of Multicomponent Adsorption Equilibria by Liquid Chromatography

Equilibrium relations for the fructose-dextran-water system on silica gel have been determined by a liquid chromatographic method. The experimental procedure discussed provides a simple and straightforward means of determining adsorption equilibria. The ternary adsorption equilibria, derived from chromatographic retention time measurements of binary systems, are verified by the equilibrium theory developed by Gluekauf (1949).

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## Introduction

The conventional method of determining multicomponent adsorption equilibria involves measuring the change in the bulk phase composition in a batch system when a known quantity of a fluid is equilibrated with a known quantity of a porous adsorbent. This batch material balance technique is experimentally tedious and time consuming and, in certain concentration ranges, is subject to large errors because the adsorbed phase composition has to be determined by difference. Another technique, the chromatographic method, involves measuring the retention time of a pulse of a solute injected into a steady stream of a carrier flowing through a column packed with the appropriate porous adsorbent. This method offers speed and simplicity and, in some cases, improved accuracy. The application of the chromatographic technique to the measurement of binary adsorption equilibria in both gas and liquid systems is fairly well established (van der Vlist and van der Meijden, 1973; Ruthven and Kumar, 1980; Hyun and Danner, 1982; Barker and Thawait, 1984; Ruthven, 1986). This paper investigates the possibility of extending the method to the determination of equilibrium relations for a ternary system.

## Theory

A perturbation in concentration propagates through a chromatographic column with a wave velocity that is determined by the equilibrium relation. In a constant-density binary liquid system or an isobaric gas phase system, continuity considerations show that only a single concentration wave will be observed and the wave velocity will be the same regardless of which of the two components is perturbed. The theory, which does not require the absence of mass transfer resistance or axial dispersion but only that the column be long enough to contain several "theoretical plates," has been presented in detail by Ruthven and Kumar (1980).

We consider a solute component, designated by subscript $i$, in a solvent, designated by subscript $s$, which is competitively adsorbed. The wave velocity and hence the retention time for a small concentration pulse is given by:

$$\omega_i = \frac{L}{\tau_i} = \frac{v}{1 + \left(\frac{1-\epsilon}{\epsilon}\right) K_i} \tag{1}$$

where

$$K_i = (1 - x_i)\frac{dq_i^*}{dc_i} + x_i \frac{dq_s^*}{dc_s} \tag{2}$$

$x_i$ is the mass fraction of the solute in the fluid phase and $dq_i^*/dc_i$, $dq_s^*/dc_s$ are the local slopes of the equilibrium curve. If the densities of the pore and fluid phases remain constant over the small concentration change, which is equivalent to assuming no net mass flux into or out of the porous adsorbent, we have:

$$\frac{dq_i^*}{dc_i} = \frac{q}{c}\frac{dy_i^*}{dx_i} \tag{3}$$

$$\frac{dq_s^*}{dc_s} = \frac{q}{c}\frac{d(1-y_i^*)}{d(1-x_i)} = \frac{dq_i^*}{dc_i} \tag{4}$$

Substituting Eq. 4 in Eq. 2 yields:

$$K_i = \frac{dq_i^*}{dc_i} \tag{5}$$

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The corresponding expressions for a variable-density system, which are slightly more complex, are derived in the appendix. It follows from Eqs. 1 and 5 that measurement of the retention time (or the wave velocity) yields directly the local slope of the equilibrium line which, subject to the constant-density approximation, is the same for both the solute and the solvent.

The simplest approach to the correlation of liquid phase equilibrium data is to represent the equilibrium in terms of a concentration-dependent distribution coefficient:

$$K_i = \frac{q_i^*}{c_i} = k_i + A_i c_i^{m_i}$$

$$\frac{dq_i^*}{dc_i} = k_i + A_i(m_i + 1)\, c_i^{m_i} \tag{6}$$

When the curvature of the equilibrium line is not too great, linear expressions of Eq. 6 ($m_i = 1$) as used by Barker and Thawait (1984) are adequate (but see Ruthven [1986] for a correction to their analysis). $k_i$ is the apparent Henry's law constant, the slope of the equilibrium line at infinite dilution. It follows immediately from Eqs. 1, 5, and 6 that $k_i$, $A_i$, and $m_i$ may easily be determined from measurements of retention time over a range of concentrations.

The situation is more complicated in a ternary mixture (component 1 and component 2 in a solvent) since, although the retention time is still given by Eq. 1 and $K_i$, subject to the constant-density approximation is still given by $dq_i^*/dc_i$ (Eq. 5), the slope of the equilibrium curve is now a function of both $c_1$ and $c_2$. The behavior of systems of this type has been examined by Glueckauf (1949), who showed that the wave velocities of the two components are given by:

$$\omega_1 = \frac{v}{1 + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{dq_1^*}{dc_1}}$$

$$\omega_2 = \frac{v}{1 + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{dq_2^*}{dc_2}} \tag{7}$$

in which:

$$\frac{dq^*{}_1}{dc_1} = \frac{\partial q_1^*}{\partial c_1} + \frac{\partial q_1^*}{\partial c_2}\frac{dc_2}{dc_1} \tag{8}$$

$$\frac{dq_2^*}{dc_2} = \frac{\partial q_2^*}{\partial c_2} + \frac{\partial q_2^*}{\partial c_1}\frac{dc_1}{dc_2} \tag{9}$$

The coherence condition requires $\omega_1 = \omega_2$, whence:

$$\frac{\partial q_2^*}{\partial c_1}\left(\frac{dc_1}{dc_2}\right)^2 + \left(\frac{\partial q_2^*}{\partial c_2} - \frac{\partial q_1^*}{\partial c_1}\right)\frac{dc_1}{dc_2} - \frac{\partial q_1^*}{\partial c_2} = 0 \tag{10}$$

Equation 10 can be regarded as a quadratic defining $dc_1/dc_2$. The two roots will give two different values of $\omega_1$ (or $\omega_2$) according to Eq. 7. These correspond to the velocities for an injected pulse of component 1 or a pulse of component 2, which in a ternary system are not the same. By measuring the retention time over a range of compositions it is therefore possible, in principle, to determine the partial gradients $\partial q_1^*/\partial c_1$, $\partial q_2^*/\partial c_1$, $\partial q_2^*/\partial c_2$, $\partial q_1^*/\partial c_2$, and hence to construct the equilibrium surfaces $q_1^*(c_1, c_2)$ and $q_2^*(c_1, c_2)$, but a completely general approach along these lines appears difficult. However, if we assume appropriate functional forms for these surfaces, containing arbitrary constants, we may determine these constants from the retention time data. This is essentially the ternary extension of the procedure suggested by van der Vlist and van der Meijden (1973).

The simplest representation of ternary equilibrium data ($c_1$, $c_2$, $c_s$) is, by direct extension of Eq. 6:

$$\frac{q_1^*}{c_1} = k_1 + A_1 c_1^{m_1} + B_{12} c_2^{n_{12}} \tag{11}$$

$$\frac{q_2^*}{c_2} = k_2 + A_2 c_2^{m_2} + B_{21} c_1^{n_{21}} \tag{12}$$

If we now consider the ternary mixture (concentrations $c_1$, $c_2$, $c_s$) subjected to a pulse of either solute, the wave velocity or retention time will be given by Eqs. 7–9 with $dc_1/dc_2$ given by Eq. 10. The partial derivatives in Eqs. 8–10 have the following forms:

$$\left(\frac{\partial q_1^*}{\partial c_1}\right)_{c_2} = k_1 + A_1(m_1 + 1)\, c_1^{m_1} + B_{12} c_2^{n_{12}} \tag{13}$$

$$\left(\frac{\partial q_1^*}{\partial c_2}\right)_{c_1} = B_{12} n_{12} c_1 c_2^{(n_{12}-1)} \tag{14}$$

$$\left(\frac{\partial q_2^*}{\partial c_2}\right)_{c_1} = k_2 + A_2(m_2 + 1)\, c_2^{m_2} + B_{21}\, c_1^{n_{21}} \tag{15}$$

$$\left(\frac{\partial q_2^*}{\partial c_1}\right)_{c_2} = B_{21} n_{21} c_2 c_1^{(n_{21}-1)} \tag{16}$$

The ten constants ($k_1$, $A_1$, $B_{12}$, $m_1$, $n_{12}$, $k_2$, $A_2$, $B_{21}$, $m_2$, $n_{21}$) may, in principle, be evaluated from ten wave velocity measurements at different compositions. However, a more convenient approach is as follows. For a pulse of component 1 in a base solution of component 2 ($c_1 = 0$), Eq. 11 becomes:

$$\frac{dq_1^*}{dc_1} = k_1 + B_{12} c_2^{n_{12}} \tag{17}$$

while for a pulse of component 2 in a base solution of component 1 ($c_2 = 0$) Eq. 12 becomes:

$$\frac{dq_2^*}{dc_2} = k_2 + B_{21} c_1^{n_{21}} \tag{18}$$

Measurements carried out over a range of compositions thus yield $k_1$, $B_{12}$, $n_{12}$, $k_2$, $B_{21}$, and $n_{21}$ directly. The values of $k_1$ and $k_2$ should of course coincide with the values from the binary system. Measurements with the binary systems (pulses of component 1 in a solution of component 1 and pulses of component 2 in a solution of component 2) and measurements with the pseudobinary systems (pulses of component 1 in a solution of component 2 and pulses of component 2 in a solution of component 1) thus yield all the parameters: $k_1$, $A_1$, $B_{12}$, $m_1$, $n_{12}$, $k_2$, $A_2$, $B_{21}$, $m_2$, and $n_{21}$. The retention times for pulses of both components 1 and 2 in a solution containing both components (a ternary system) can then be predicted from Eq. 7 with $dq_1^*/dc_1$ and $dq_2^*/dc_2$ cal-

**Table 1. Details of Column and Porous Adsorbent**

| | |
|---|---|
| Column length, cm | 13 |
| Column diameter, cm | 1.6 |
| Porous adsorbent | silica gel |
| Particle size, μm | 425–500 |
| Mean pore diameter, Å | 37 |
| Porosity | 0.65 |
| Specific area, cm$^2$/g | $6.51 \times 10^6$ |
| Specific pore volume, cm$^3$/g | 0.806 |

culated from Eqs. 8–10 and 13–16. A comparison with the measured retention times can then be made to test the validity of the assumption that the constants derived from the binary data are applicable to the ternary system.

## Experimental Method

The method outlined above was used to investigate equilibrium in the system fructose-dextran-water (component 1–component 2–solvent) on silica gel. The porous adsorbent was purchased from Fluka Chemie AG. It was characterized by low-temperature nitrogen adsorption, measured using a Quantasorb instrument. Details of the physical properties are summarized in Table 1. Dextran of mean molecular weight 6000, designated T6, was obtained from the same source while dextran of mean molecular weight 9400, designated T9, and fructose of standard reagent grade were supplied by Sigma Chemical Company.

The chromatographic system utilized a Varian HPLC pump to provide a steady flow of liquid through the column, which was a standard Pharmacia jacketed glass column of dimensions given in Table 1, to a refractive index detector (Hewlett-Packard 1037A). The sample injection valve was a standard LC valve (Rheodyne 7125) with a 200 μL sample loop. The millivolt signal from the detector was converted to digital form with the aid of a Hewlett Packard 3497A data acquisition unit interfaced with a microcomputer for data storage and processing. All experiments were carried out under thermostatic conditions at 25°C. The column voidage was determined by injection of a pulse of blue dextran, a very high molecular weight species that will not penetrate the small pores of the gel particles.

Retention time measurements for the binary and pseudobinary systems were performed as follows:

I. Pulses of fructose, dextran T6, and dextran T9 were injected into an eluent containing 0–0.38 g/cm$^3$ fructose.

II. Pulses of fructose, dextran T6, and dextran T9 were injected into a solution containing 0–0.34 g/cm$^3$ dextran T6.

III. Pulses of fructose, dextran T6, and dextran T9 were injected into a solution containing 0–0.25 g/cm$^3$ dextran T9.

The injected pulse in the above three cases was a solution of composition similar to the eluent but with a slightly higher concentration of fructose, dextran T6, or dextran T9. Similarly, retention time measurements were performed for the three components combined to form the ternary systems listed in Table 2. The injected sample solution consisted of the eluent with an increased concentration of fructose, dextran T6, or dextran T9.

The response curves were integrated numerically in order to determine the first moments and hence the mean retention times:

$$\mu = \frac{\int_0^\infty ct\, dt}{\int_0^\infty c\, dt} \tag{19}$$

The correction for dead volume was determined from a pulse response measurement with the column removed from the system and the injector connected directly to the detector.

## Results and Discussion

The column voidage, $\epsilon$, was determined from retention time measurements with blue dextran, a molecule too large to penetrate the pores of the adsorbent. The distribution coefficient $K$ for blue dextran is thus zero and Eq. 1 is reduced to:

$$\tau = \frac{L}{u}\epsilon \tag{20}$$

The retention times were measured for blue dextran over a range of eluent flow rates and plotted against $L/u$, as shown in Figure 1. The slope of the linear plot yields $\epsilon = 0.45$.

The retention time measurements with pulses of fructose, dextran T6, and dextran T9 injected into an eluent containing fructose were used to calculate the local slopes of the binary equilibrium relations $dq_F^*/dc_F$, $dq_{T6}^*/dc_{T6}$, and $dq_{T9}^*/dc_{T9}$ according to Eq. 1. No density correction was applied since, as shown in the appendix, the density correction factor is in fact close to unity under the experimental conditions employed in this study. The calculated $dq_i^*/dc_i$ values were plotted against the fructose concentration, as shown in Figure 2. The relationship is essentially linear for each solute and the best fit lines were found by the method of least squares. Hence, according to Eq. 6 with $m_F = 1$ for a linear fit, the intercept and the slope of the plot for fructose yield $k_F$ and $2A_F$, respectively. Similarly, the parameters $k_{T6}$, $B_{T6F}$, $k_{T9}$, and $B_{T9F}$ were determined from the intercepts and the slopes of the plots for dextran T6 and dextran T9 in Figure 2, respectively, according to Eq. 18 with both $n_{T6F}$ and $n_{T9F}$ set to one. Figures 3 and 4 show the $dq_i^*/dc_i$ values for the three solutes plotted against dextran T6 and dextran T9 concentrations. The data in both figures, showing curvature in the low concentration range, were fitted according to the equilibrium relations of Eqs. 6, 17, and 18 as follows:

I. *Pulses of a solute injected into a base solution containing the same solute.*

**Table 2. Ternary Systems Composed from the Three Components**

| System | Solutes 1 and 2 in Eluent | Concentration of Solutes 1 and 2 g/cm$^3$ | Injected Component |
|---|---|---|---|
| I | Fructose/dextran T6 | 0.29/0.145 | Fructose/dextran T6 |
| II | Fructose/dextran T9 | 0.29/0.145 | Fructose/dextran T9 |
| III | Dextran T6/dextran T9 | 0.1/0.1 | Dextran T6/dextran T9 |

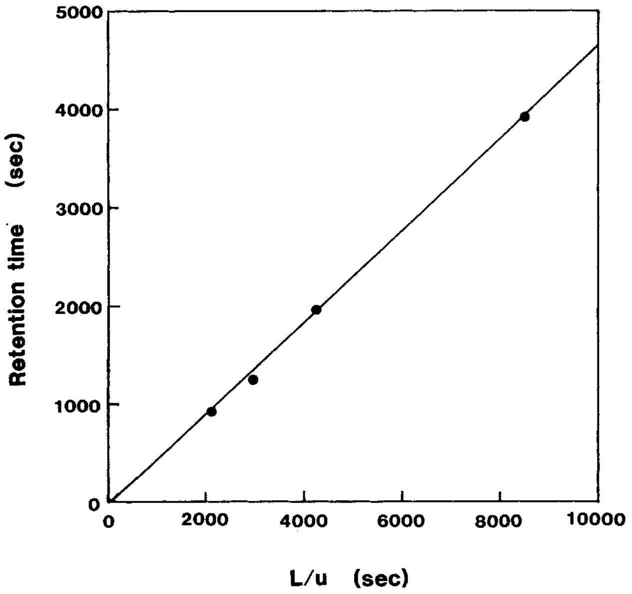

Figure 1. Retention time vs. $L/u$ for blue dextran.

Since the distribution coefficients at infinite dilution $k_{T6}$ and $k_{T9}$ have been determined previously, Eq. 6 may be rewritten in the following form:

$$\ln\left(\frac{dq_i^*}{dc_i} - k_i\right) = \ln A_i(m_i + 1) + m_i \ln c_i \tag{21}$$

The data for dextran T6 injected into a base solution of dextran

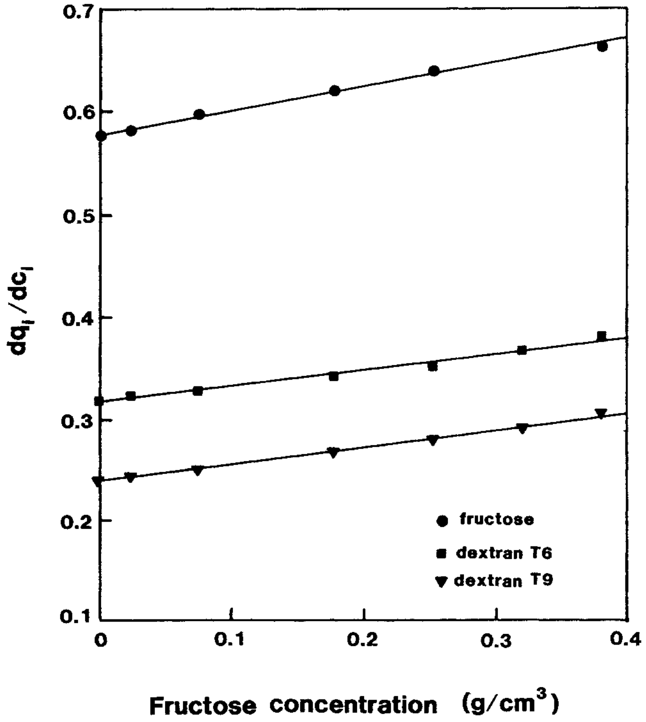

Figure 2. Local slopes of equilibrium relations ($dq_i^*/dc_i$) for fructose, dextran T6, and dextran T9 vs. fructose concentrations.

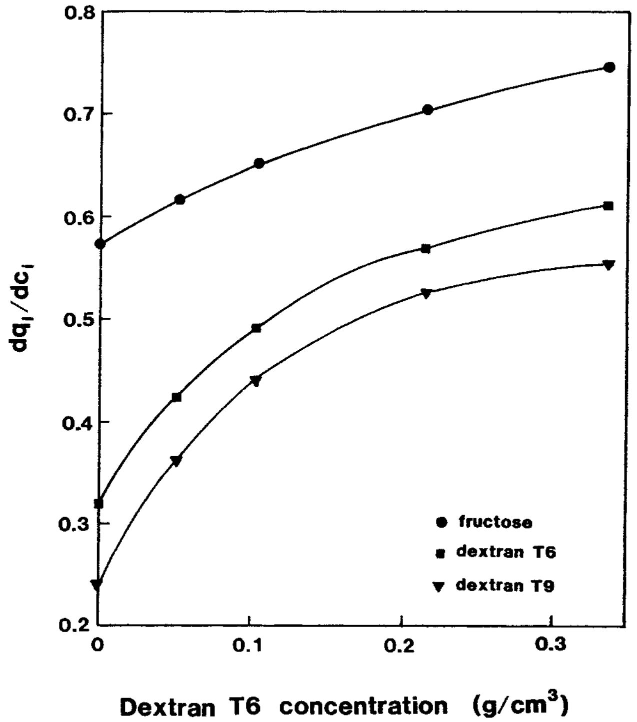

Figure 3. Local slopes of equilibrium relations ($dq_i^*/dc_i$) for fructose, dextran T6, and dextran T9 vs. dextran T6 concentrations.

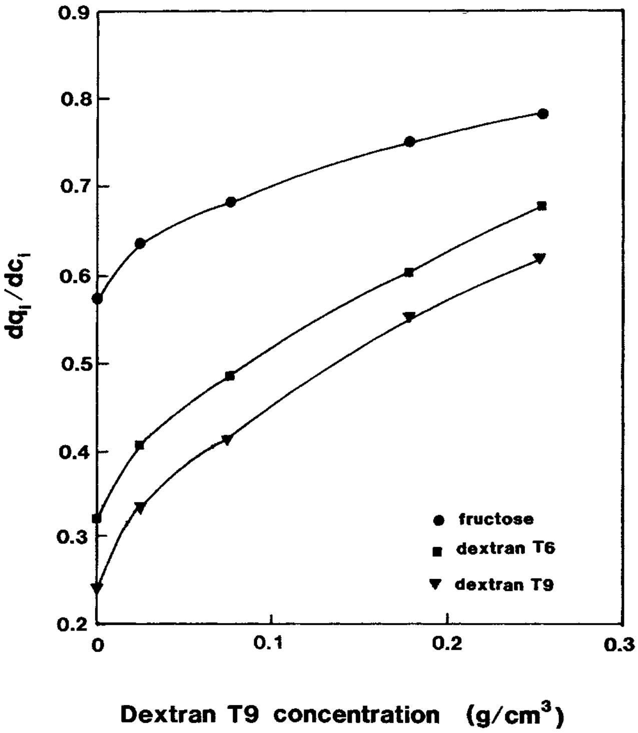

Figure 4. Local slopes of equilibrium relations ($dq_i^*/dc_i$) for fructose, dextran T6, and dextran T9 vs. dextran T9 concentrations.

T6 (Figure 3) and dextran T9 injected into a base solution containing dextran T9 (Figure 4) were plotted according to Eq. 21, as shown in Figure 5. The slopes of these linear plots yield $m_{T6}$ and $m_{T9}$ directly while the intercepts give $A_{T6}$ and $A_{T9}$.

II. *Pulses of a solute injected into a base solution containing a different solute.*

The equilibrium relations for these cases are represented by Eq. 17 or 18. Using the same approach as in I above, the data for fructose and dextran T9 injected into a base solution of dextran T6, as shown in Figure 3, were analyzed according to the following equation:

$$\ln\left(\frac{dq_i^*}{dc_i} - k_i\right) = \ln B_{iT6} + n_{iT6} \ln c_{T6} \qquad (22)$$

while the data for fructose and dextran T6 injected into a base solution of dextran T9, as shown in Figure 4, were analyzed according to Eq. 23:

$$\ln\left(\frac{dq_i^*}{dc_i} - k_i\right) = \ln B_{iT9} + n_{iT9} \ln c_{T9} \qquad (23)$$

**Table 3. Equilibrium Relations for Fructose, Dextran T6, and Dextran T9**

| Eluent Medium | Injected Component | Equilibrium Relation | Correlation Coefficient |
|---|---|---|---|
| Fructose | Fructose | $\frac{q_F}{c_F} = k_F + A_F c_F$<br>$= 0.575 + 0.122\, c_F$ | 0.9932 |
| | Dextran T6 | $\frac{q_{T6}}{c_{T6}} = k_{T6} + B_{T6F} c_F$<br>$= 0.317 + 0.155\, c_F$ | 0.9710 |
| | Dextran T9 | $\frac{q_{T9}}{c_{T9}} = k_{T9} + B_{T9F} c_F$<br>$= 0.238 + 0.163\, c_F$ | 0.9821 |
| Dextran T6 | Fructose | $\frac{q_F}{c_F} = k_F + B_{FT6} c_{T6}^{n_{FT6}}$<br>$= 0.575 + 0.399\, c_{T6}^{0.636}$ | 0.9960 |
| | Dextran T6 | $\frac{q_{T6}}{c_{T6}} = k_{T6} + A_{T6} c_{T6}^{m_{T6}}$<br>$= 0.317 + 0.363\, c_{T6}^{0.546}$ | 0.9840 |
| | Dextran T9 | $\frac{q_{T9}}{c_{T9}} = k_{T9} + B_{T9T6} c_{T6}^{n_{T9T6}}$<br>$= 0.238 + 0.592\, c_{T6}^{0.507}$ | 0.9697 |
| Dextran T9 | Fructose | $\frac{q_F}{c_F} = k_F + B_{FT9} c_{T9}^{n_{FT9}}$<br>$= 0.575 + 0.428\, c_{T9}^{0.510}$ | 0.9979 |
| | Dextran T6 | $\frac{q_{T6}}{c_{T6}} = k_{T6} + B_{T6T9} c_{T9}^{n_{T6T9}}$<br>$= 0.317 + 0.816\, c_{T9}^{0.603}$ | 0.9978 |
| | Dextran T9 | $\frac{q_{T9}}{c_{T9}} = k_{T9} + A_{T9} c_{T9}^{m_{T9}}$<br>$= 0.238 + 0.521\, c_{T9}^{0.565}$ | 0.9862 |

Table 3 summarizes the equilibrium parameters for each solute. Using the equilibrium parameters derived from the binary data, the retention times for fructose and dextran T6 in an aqueous ternary solution containing 0.29 g/cm$^3$ fructose and 0.145 g/cm$^3$ dextran T6 (system I in Table 2) were calculated according to Eqs. 7–10 and 13–15. These values are compared in Table 4 with the experimentally measured retention times for this solution. The same procedure was used for the fructose–dextran T9–water system (system II in Table 2) and for the dextran T6–dextran T9–water system (system III in Table 2). In all three cases there is good agreement between the predicted and measured retention times, confirming that the equilibrium data for the ternary system conform to the predictions derived from the binary data.

The results shown in Table 3 indicate that the distribution coefficients for the three components increase with increasing bulk phase concentration but the rate of change is larger for the two dextran species than for fructose ($A_{T6}$ and $A_{T9} > A_F$). Since changes in the solution density are modest, the concentration dependence of the distribution coefficient must arise from either sorbate-sorbate or sorbate-pore wall interactions (Anderson and Brannon, 1981; Glandt, 1981). Such effects may be expected to be more pronounced for dextran, a flexible polymer, than for fructose, a comparatively compact and rigid molecule (Brannon and Anderson, 1982). On that basis the observed difference in

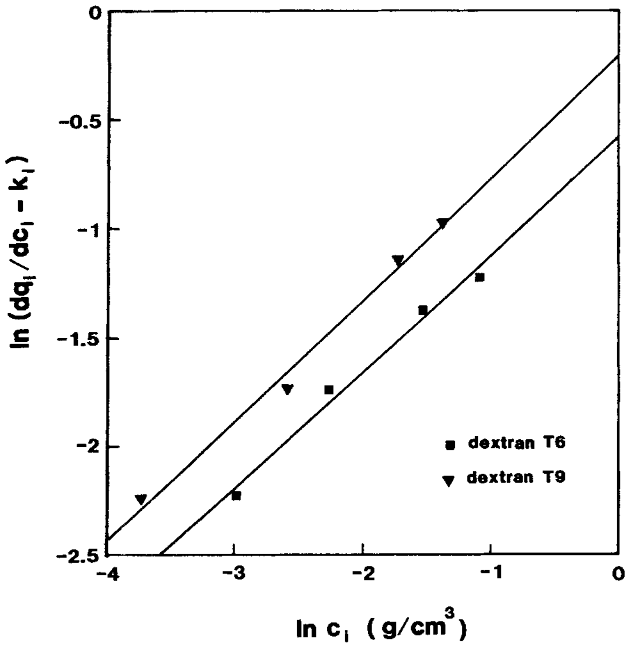

**Figure 5. Plots for dextran T6 and dextran T9 according to Eq. 21.**

**Table 4. Theoretical and Experimental Retention Times for the Ternary Systems (Table 2)**

| Ternary System | Injected Component | Retention Time,* min. | |
|---|---|---|---|
| | | Theory | Exp. |
| I | Fructose | 75.43 | 75.21 |
| | Dextran T6 | 65.02 | 66.61 |
| II | Fructose | 78.63 | 77.17 |
| | Dextran T9 | 65.48 | 67.09 |
| III | Dextran T6 | 74.06 | 73.33 |
| | Dextran T9 | 63.30 | 63.73 |

Eluent flow rate, 0.3 cm$^3$/min

behavior is qualitatively understandable although there exists no proper basis for quantitative predictions.

## Conclusions

Chromatographic retention time measurements provide a simple and straightforward means of determining binary adsorption equilibria but this approach cannot be directly extended to ternary and multicomponent system since, in such systems, the key derivatives $dq_i^*/dc_i$ depend on the concentration changes for all components. A partial solution to this problem has been developed here based on the assumption that the sorbate–sorbate interactions in the ternary are the same as in the constituent binaries. The validity of this assumption is then confirmed by comparing, for a limited number of compositions, the predicted and measured retention times in the ternary system. If there is agreement, as found in the present study for the fructose–dextran T6, fructose–dextran T9, and dextran T6–dextran T9 systems, one may have some confidence in using the predictions from the binary data over a wide range of ternary compositions. However, the approach is obviously restricted to cases in which ternary interaction effects can be neglected and it provides no information as to how to proceed in instances where the predicted and measured retention times in the ternary do not agree. Nevertheless, the much higher statistical weight of binary interactions relative to three-body interactions ensures that in most practical systems this approach will be successful since the binary interactions are normally dominant.

## Notation

$A$ = equilibrium parameter, Eq. 6
$B$ = equilibrium parameter, Eqs. 11, 12, cm$^3$/g
$c$ = solute concentration in bulk phase, g/cm$^3$
$k$ = equilibrium parameter, Eqs. 6, 11, 12
$K$ = distribution coefficient
$L$ = packed length of column, cm
$m$ = equilibrium parameter, Eq. 6
$n$ = equilibrium parameter, Eqs. 11, 12
$q$ = solute concentration based on particle volume, g/cm$^3$
$t$ = time, s
$u$ = superficial fluid velocity, cm/s
$v$ = interstitial fluid velocity, cm/s
$x$ = solute mass fraction in bulk phase
$x'$ = small change in solute mass fraction about an initially established equilibrium composition
$X$ = equilibrium solute mass fraction in bulk phase
$y$ = solute mass fraction in pore
$z$ = axial distance, cm

### *Greek letters*

$\alpha$ = density correction factor, Eq. A19
$\beta$ = $(1 - \epsilon)/\epsilon$
$\epsilon$ = voidage of packed bed
$\epsilon_p$ = particle porosity
$\rho$ = solution density of bulk phase, g/cm$^3$
$\rho'$ = solution density in pore, g/cm$^3$
$\omega$ = velocity of equilibrium front, cm/s

### *Superscript*

$*$ = equilibrium value

### *Subscripts*

F = fructose
$i$ = fructose, dextran T6, or dextran T9
$s$ = solvent
T6 = dextran T6
T9 = dextran T9

## Appendix

The fundamental differential mass balance equation for an element of a chromatographic column with plug flow (dispersed plug flow model leads to similar results) is:

$$v\frac{\partial c_i}{\partial z} + c_i\frac{\partial v}{\partial z} + \frac{\partial c_i}{\partial t} + \beta\frac{\partial q_i}{\partial t} = 0 \tag{A1}$$

where $\beta = (1 - \epsilon)/\epsilon$.

It is convenient to recast Eq. A1 in terms of mass fraction and solution density when the density varies with the mass fraction.

$$c_i = \rho x_i \tag{A2}$$

$$q_i = \rho' y_i \epsilon_p \tag{A3}$$

$$\frac{\partial \rho}{\partial z} = \frac{d\rho}{dx_i}\frac{\partial x_i}{\partial z}, \quad \frac{\partial \rho}{\partial t} = \frac{d\rho}{dx_i}\frac{\partial x_i}{\partial t}, \quad \frac{\partial \rho'}{\partial t} = \frac{\partial \rho'}{dy_i}\frac{\partial y_i}{\partial t} \tag{A4}$$

Substitution of Eqs. A2–A4 in Eq. A1 yields:

$$v\left(\rho + x_i\frac{d\rho}{dx_i}\right)\frac{\partial x_i}{\partial z} + \rho x_i\frac{\partial v}{\partial z} + \left(\rho + x_i\frac{d\rho}{dx_i}\right)\frac{\partial x_i}{\partial t} + \beta\epsilon_p\left(\rho' + y_i\frac{d\rho'}{dy_i}\right)\frac{\partial y_i}{\partial t} = 0 \tag{A5}$$

For an aqueous system such as fructose–water or dextran–water one has an equation of this form for both the solute and the solvent. The subsequent development outlined here is based on the dextran T9–water system.

$$v\left(\rho + x_{T9}\frac{d\rho}{dx_{T9}}\right)\frac{\partial x_{T9}}{\partial z} + \rho x_{T9}\frac{\partial v}{\partial z} + \left(\rho + x_{T9}\frac{d\rho}{dx_{T9}}\right)\frac{\partial x_{T9}}{\partial t} + \beta\epsilon_p\left(\rho' + y_{T9}\frac{d\rho'}{dy_{T9}}\right)\frac{\partial y_{T9}}{\partial t} = 0 \tag{A6}$$

$$v\left(\rho + x_s\frac{d\rho}{dx_s}\right)\frac{\partial x_s}{\partial z} + \rho x_s\frac{\partial v}{\partial z} + \left(\rho + x_s\frac{d\partial}{dx_s}\right)\frac{\partial x_s}{\partial t} + \beta\epsilon_p\left(\rho' + y_s\frac{d\rho'}{dy_s}\right)\frac{\partial y_s}{\partial t} = 0 \tag{A7}$$

Multiplying Eq. A6 by $(1 - x_{T9})$ and Eq. A7 by $x_{T9}$ (rewriting Eq. 7 in terms of $x_{T9}$ and $y_{T9}$ using $x_{T9} + x_s = 1$ and $y_{T9} + y_s = 1$), subtracting we obtain:

$$v\rho\frac{\partial x_{T9}}{\partial z} + \rho\frac{\partial x_{T9}}{\partial t} + \beta\epsilon_p\left(\rho' + (y_{T9} - x_{T9})\frac{d\rho'}{dy_{T9}}\right)\frac{\partial y_{T9}}{\partial t} = 0 \tag{A8}$$

For small changes, $x'$, about an initially established equilibrium composition, $x_{T9}$, Eq. A8 becomes:

$$v\frac{\partial x'}{\partial z} + \frac{\partial x'}{\partial t} + \beta\epsilon_p\left[\frac{\rho'}{\rho} + \frac{(y_{T9}^* - X_{T9})}{\rho}\frac{d\rho'}{dy_{T9}}\right]\frac{\partial y_{T9}^*}{\partial t} = 0 \tag{A9}$$

The equilibrium relationship may be taken to be linear for small changes in composition:

$$y^*_{T9} = \left(\frac{dy^*_{T9}}{dX_{T9}}\right) X_{T9} + \text{constant} \qquad \text{(A10)}$$

To obtain the velocity of the equilibrium concentration front we put:

$$\frac{\partial y^*_{T9}}{\partial t} = \left(\frac{dy^*_{T9}}{dX_{T9}}\right)\frac{\partial X_{T9}}{\partial t} = \left(\frac{dy^*_{T9}}{dX_{T9}}\right)\frac{\partial x'}{\partial t} \qquad \text{(A11)}$$

which gives

$$v\frac{\partial x'}{\partial z} + \frac{\partial x'}{\partial t}\left\{1 + \beta\epsilon_p\left[\frac{\rho'}{\rho} + \frac{(y^*_{T9} - X_{T9})}{\rho}\frac{d\rho'}{dy_{T9}}\right]\frac{dy^*_{T9}}{dX_{T9}}\right\} = 0 \qquad \text{(A12)}$$

Equation A12 has the form of the kinematic wave equation. The velocity with which the concentration front propagates through the column is given by:

$$\omega = \frac{v}{\left\{1 + \beta\epsilon_p\left[\frac{\rho'}{\rho} + \frac{(y^*_{T9} - X_{T9})}{\rho}\frac{d\rho'}{dy_{T9}}\right]\frac{dy^*_{T9}}{dX_{T9}}\right\}} \qquad \text{(A13)}$$

The variation of the dextran T9 solution density with mass fraction in the range of 0 to 40 wt.% was measured with a digital density meter (model no. DMA46, Anton Paar KG, Graz/Austria). Linear regression gives the following equation:

$$\rho \text{ or } \rho' = 0.9933 + 0.4292\,(x_{T9} \text{ or } y_{T9}) \qquad \text{(A14)}$$

Using Eq. A14 we can express concentrations ($c_{T9}$ and $q_{T9}$) in terms of mass fractions:

$$c_{T9} = \rho x_{T9} = 0.9933\,x_{T9} + 0.4292\,x^2_{T9} \qquad \text{(A15)}$$

$$q_{T9} = \rho' y_{T9}\epsilon_P = (0.9933\,y_{T9} + 0.4292\,y^2_{T9})\epsilon_p \qquad \text{(A16)}$$

Putting $x_{T9} = X_{T9}$ and differentiating Eqs. A15 and A16 we get:

$$\epsilon_p\frac{dy^*_{T9}}{dX_{T9}} = \frac{dq^*_{T9}}{dc_{T9}}\left(\frac{0.9933 + 0.8584X_{T9}}{0.9933 + 0.8584y^*_{T9}}\right) \qquad \text{(A17)}$$

Substitution of Eq. A17 in Eq. A13 yields:

$$\omega = \frac{v}{\left(1 + \alpha_{T9}\beta\frac{dq^*_{T9}}{dc_{T9}}\right)} \qquad \text{(A18)}$$

**Table 5. Estimated Values of Density Correction Factors $\alpha_F$, $\alpha_{T6}$, and $\alpha_{T9}$**

| $x_i$ | $y^*_F$ | $\alpha_F$ | $y^*_{T6}$ | $\alpha_{T6}$ | $y^*_{T9}$ | $\alpha_{T9}$ |
|---|---|---|---|---|---|---|
| 0.1 | 0.0908 | 0.9997 | 0.0170 | 0.9972 | 0.0599 | 0.9979 |
| 0.2 | 0.1861 | 0.9991 | 0.1488 | 0.9970 | 0.1439 | 0.9966 |
| 0.3 | 0.2860 | 0.9995 | 0.2269 | 0.9942 | 0.2450 | 0.9955 |
| 0.4 | 0.3904 | 0.9990 | 0.3483 | 0.9952 | 0.3600 | 0.9961 |

where

$$\alpha_{T9} = \left[\frac{\rho'_{T9}}{\rho_{T9}} + \frac{(y^*_{T9} - X_{T9})}{\rho_{T9}}\frac{d\rho'_{T9}}{dy_{T9}}\right]\left(\frac{0.9933 + 0.8584X_{T9}}{0.9933 + 0\,.8584y_{T9}}\right) \qquad \text{(A19)}$$

The mean retention time is thus given by:

$$\tau = \frac{L}{v}\left(1 + \alpha_{T9}\beta\frac{dq^*_{T9}}{dc_{T9}}\right) \qquad \text{(20)}$$

In order to estimate the density correction factors $\alpha_{T9}$ (Eq. A19) in the dextran T9–water system, we first estimate the adsorbed phase mass fraction $y_{T9}$. The $dq_{T9}/dc_{T9}$ vs. $c_{T9}$ plot, Figure 4, gives the following equation with the assumption of $\alpha_{T9} = 1$:

$$\frac{q_{T9}}{c_{T9}} = 0.238 + 0.521\,c^{0.565}_{T9} \qquad \text{(A21)}$$

Using Eqs. A15, A16, and A21 we can estimate $y^*_{T9}$ for known values of $x_{T9}$. The estimated values of $\alpha_{T9}$ are tabulated in Table 5. The values of $\alpha_F$ and $\alpha_{T6}$ in Table 5 were estimated using the approach outlined above.

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