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Separation of Isomers via Thermal Parametric Pumping

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A recent series of experimental investigations by Chen et al. (1972, 1973, 1974a, 1974b, 1974c) has shown that continuous and semicontinuous parametric pumping can yield very high separation factors in small equipment in a relatively short period of time. In this note we extend our investigation to the separation of isomers. The model system studied is glucose-fructose-water on a cation exchanger (Bio-Rad AG 50W-X4, calcium form). A comparison is made between the experimental data and the calculated results based on the method proposed by Chen et al. (1974a). It should be pointed out that sugar mixtures are notoriously difficult to separate (Hatt and Triffett, 1965) and there has never been a thorough study done on the separation of glucose and fructose even though it might be advantageous industrially in the manufacture of fructose from sucrose via invert sugar.

EXPERIMENT

The experimental apparatus was the same as that used previously (Chen et al., 1972). The feed solution was prepared using reagent grade fructose and glucose obtained from Fisher Scientific Company. Samples for analysis were taken from the product streams at the end of each cycle and analyzed by an automatic polarimeter. For runs involving the binary systems (glucose-water and fructose-water), the analysis was straightforward and the concentration of solute was linearly proportional to the polarimeter reading expressed in angular degree, that is, $R_g{}^0 = \beta_g \eta_g$ for glucose and $R_f{}^0 = \beta_f \eta_f$ for fructose (curves 1 and 2 of Figure 1). In the case of the ternary system, glucose-fructose-water, the analysis was somewhat complicated. The R^0 for total sugars (glucose and fructose) was assumed to be the sum of that for glucose and for fructose, that is,

$$R^0 = R_g{}^0 + R_f{}^0$$

$$R^0 = \beta_f \eta + \eta_g(\beta_g - \beta_f) \qquad (1)$$

where

$$\eta = \eta_g + \eta_f$$

$$\beta_g = 9.614 \times 10^3$$

$$\beta_f = -16.796 \times 10^3$$

As shown in Equation (1), for a given η_g, a straight line results when R^0 is plotted against η (curve 3 of Figure 1). Thus, knowing η_g one can determine η from R^0 using Equation (1), and the fructose concentration η_f is obtained by subtraction of η_g from η. Note that η_g may be determined by the use of glucostat (Teller, 1956). However, for the present study η_g was found to be constant and equal to the feed concentration (see Results and Discussion).

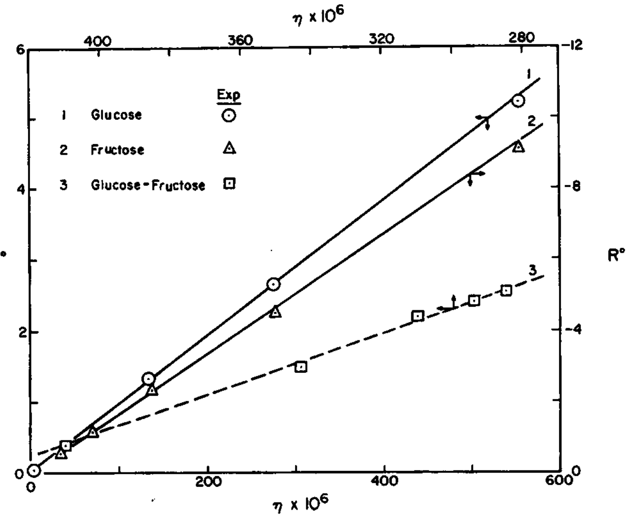

Fig. 1. Relation of angular degree rotation to concentration at ambient temperature (For curve 3, $\eta_g = 277.3 \times 10^{-6}$ g moles/cc).

RESULTS AND DISCUSSION

The experimental parameters are shown in Table 1 and the data are plotted in Figures 2 to 4. The equations previously derived (Chen et al., 1972, 1973) were used to calculate the concentration transients, and computed results corresponding to the experimental runs are also plotted in Figures 2 to 4. These results compare reasonably well with the observed values for both continuous and semicontinuous pump operations. For continuous pump the feed and product streams flow steadily both in upflow and downflow cycles, while the semicontinuous pump is operated batch-wise during upflow and continuously during downflow.

Figure 2 illustrates concentration transients for both glucose and fructose in water. For glucose $\langle y_{TP2} \rangle_n / y_0$

TABLE 1. EXPERIMENTAL AND MODEL PARAMETERS

$$\frac{\pi^*}{\omega} = 1{,}200\text{ s}, T_1 = 328°\text{K}, T_2 = 278°\text{K}, b_g = 0, b_f = 0.058$$

$$h = 0.9\text{ m}, C_1 = 0.272, C_2 = 0.272, Q\left(\frac{\pi}{\omega}\right) = 25\text{ cm}^3$$

$$y_{og}^{**} = 1.423 \times 10^{-4}\text{ g moles/cm}^3,$$
$$y_{of}^{***} = 1.423 \times 10^{-4}\text{ g moles/cm}^3$$

		ϕ_B	$\phi_T + \phi_B$	$L_{1f}(m)$	$L_{2f}(m)$	$\frac{\langle y_{TP2}\rangle_\infty}{y_0}$
1. Glucose-water	Semicontinuous	0.032	0.40	—	—	—
2. Fructose-water	Semicontinuous	0.032	0.40	0.633	0.582	1.09
3. Glucose-fructose-water	Semicontinuous	0.032	0.20	0.633	0.582	1.19
4. Glucose-fructose-water	Semicontinuous	0.060	0.28	0.636	0.600	1.27
5. Glucose-fructose-water	Continuous	0.030	0.28	0.614	0.580	1.12
6. Glucose-fructose-water	Continuous	0.056	0.28	0.596	0.593	1.25
7. Glucose-fructose-water	Semicontinuous	0.080	0.20	0.633	0.609	1.67
8. Glucose-fructose-water	Continuous	0.056	0.20	0.600	0.598	1.39

* Except Run 6 for which $\frac{\pi}{\omega} = 1{,}800$ s.

** For Run 1, $y_{og} = 2.774 \times 10^{-4}$ g moles/cm³.

*** For Run 2, $y_{of} = 2.601 \times 10^{-4}$ g moles/cm³.

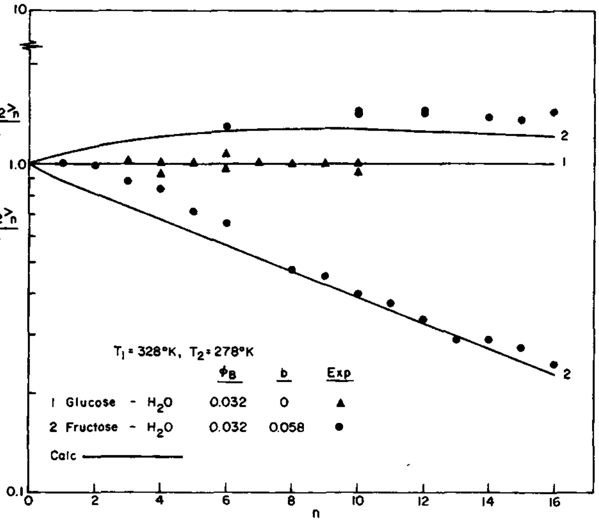

Fig. 2. Concentration transients for binary systems.

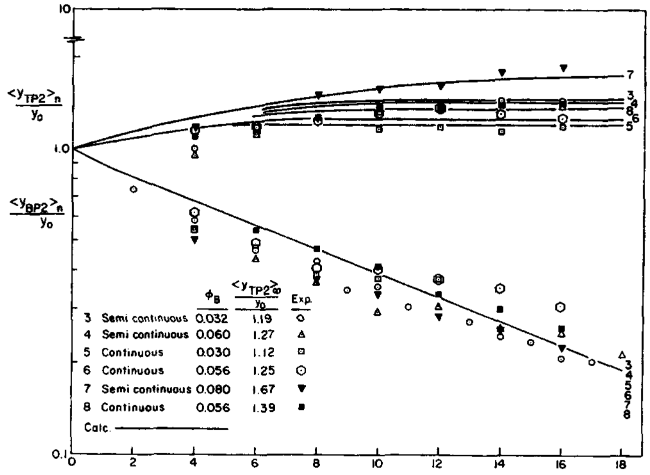

Fig. 3. Concentration transients for ternary systems.

and $\langle y_{BP2}\rangle_n/y_0$ are essentially independent of n. This means that the separation of glucose from water does not occur to any appreciable extent, and the concentrations of top and bottom product streams may be considered to be constant and equal to the feed concentration. In other words, the equilibrium distribution between glucose and the resin is insensitive to temperature and the equilibrium parameter $b_g = 0$ (Chen and Hill, 1971). For the case of fructose-water, $\langle y_{BP2}\rangle_n/y_0$ decreases as n increases, and as the theory predicts, approaches zero as n becomes large. As $n \rightarrow \infty$, fructose removal from the bottom product stream can be complete and the top product stream must carry away all of the fructose supplied by the feed stream and reach a steady state value, $\langle y_{TP2}\rangle_\infty/y_0$. Consequently, b_f can be obtained by a method described by Chen et al. (1972) and was found to be 0.058. Note that b_i is a function of hot and cold temperatures only.

Figure 3 shows the concentration transients for fructose in ternary systems (glucose-fructose-water). In the computations it is assumed that the system contains two pseudobinaries, each binary consisting of one solute as one component and the common solvent as the other component (that is, glucose-water and fructose-water). Each

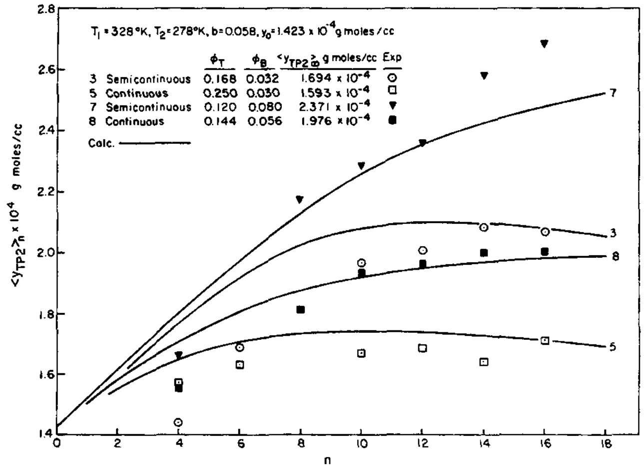

Fig. 4. Effects of operating conditions on the top product.

system could be characterized by a dimensionless equilibrium parameter b_i and corresponding values of L_{1i} and L_{2i} (Chen et al., 1974a). One can see that for all cases $\langle y_{BP2}\rangle_n/y_0$ decreases as n increases. The slope α (of Log $\langle y_{BP2}\rangle_n/y_0$ versus n) is coincident with that in the binary mixture (fructose-water, Figure 2) since α depends only on the values of C_2 and b_i, where C_2 is defined as the ratio of dead volume of the bottom reservoir to the displacement.

Chen and Hill (1971) have shown that there are three possible regions of pump operations. Regions 1, 2, and 3, depending on the relative magnitudes of penetration distances L_{1i} and L_{2i}, and the height of the column h. As long as

$$b_g < \phi_B \leq b_f \quad \text{and} \quad L_{2f} \leq h \qquad (2)$$

for the continuous pump and

$$\left(\frac{2b}{1-b}\right)_g < \phi_B \leq \left(\frac{2b}{1-b}\right)_f \quad \text{and} \quad L_{2f} \leq h \qquad (3)$$

for the semicontinuous pump, the operation is in Region 1 for fructose and Region 2 for glucose. At steady state ($n \rightarrow \infty$) fructose appears only in the top product stream, but glucose would appear in both top and bottom product streams. However, as stated before, for the present study $b_g = 0$, and the glucose concentration in either top or bottom product stream is identical to that of the feed.

It should be emphasized that the performance characteristics of both continuous and semicontinuous pumps are similar in nature. The main difference between the two pumps is the difference in the loci of switching points between Regions 1 and 2 (Chen and Hill, 1971). For the continuous pump, the switching points correspond to the condition $\phi_B = b_i$. In the case of the semicontinuous pump, the condition is $\phi_B = 2b_i/(1 - b_i)$.

Figure 4 shows the effects of ϕ_T and ϕ_B on the degree of enrichment in the top product stream. ϕ_T and ϕ_B are defined as the ratios of the top and bottom product flow rates to the reservoir displacement rate. Provided that the pumps are operated in Region 1 [see Equations (2) and (3)], the top product concentration at $n \rightarrow \infty$ would be $\langle y_{TP2}\rangle_\infty / y_0 = 1 + \phi_B/\phi_T$. As ϕ_B increases, $\langle y_{TP2}\rangle_\infty / y_0$ increases. Furthermore, for a given value of ϕ_B, by adjustment of ϕ_T to an arbitrarily low value, one may obtain an arbitrarily high value of $\langle y_{TP2}\rangle_\infty / y_0$.

NOTATION

b = equilibrium parameter, dimensionless
C_1 = top reservoir dead volume/displacement, dimensionless
C_2 = bottom reservoir dead volume/displacement, dimensionless
h = column height, m
L_1 = penetration distance for hot cycle, m
L_2 = penetration distance for cold cycle, m
n = number of cycles of pump operation
Q = reservoir displacement rate, cm^3/s
R^0 = polarimeter reading, angular degree
T_1 = column temperature during upflow, °K
T_2 = column temperature during downflow, °K
y_0 = initial or feed concentration of solute, g moles/cm^3
$\langle y_{BP2}\rangle_n$ = average bottom product concentration of solute during downflow at nth cycle, g moles/cm^3
$\langle y_{TP2}\rangle_n$ = average top product concentration of solute during downflow at nth cycle, g moles/cm^3
η = concentration, g mole/cm^3
β = R^0/η
ϕ_B = bottom product volumetric flow rate over reservoir displacement rate, dimensionless
ϕ_T = top product volumetric flow rate over reservoir displacement rate, dimensionless
π/ω = duration of half cycle, s

Subscripts

f = fructose
g = glucose
i = solute i
∞ = steady state

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Further Considerations on the Danckwerts-Gillham Method for Design of Gas Absorbers

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In a recent paper, Charpentier and Laurent (1974) recall a method proposed by Danckwerts and Gillham (1966) for prediction of the effect of a chemical reaction on the overall rate of gas absorption. The aim of this note is to clarify some characteristics and limitations of such a method.

Both experiments and theory indicate there are two sets of factors in the design of absorption equipment: the physico-chemical characteristics and the hydrodynamics of the system. Any design method must be based on similarities of both.

The stirred cell model proposed by Dankwerts (1966)