Sucrose Inversion by Partially Deactivated Ion Exchange Resin Beds

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The inversion of sucrose by partially deactivated ion exchange resin catalysts has been studied in a fixed bed reactor under conditions where intraparticle diffusion of sucrose is slow. Results show that the reaction remains apparently first order for deactivated catalyst. Activity is directly related to hydrogen content of the resin and is also dependent on the nature of the ion used to poison the catalyst.

The inversion of aqueous sucrose solutions by fixed beds of ion exchange resin has been the subject of recent studies by Reed and Dranoff (*1*), O'Connell (*2*), and Lifshutz and Dranoff (*3*). These investigations, made with completely acidified cationic resins, have shown that the reaction is first order with respect to sucrose at moderate concentrations and temperatures and is strongly influenced by intraparticle diffusion of reactant sucrose.

The present study was initiated to extend the understanding of this reaction to the case of partially deactivated catalyst. Data obtained with deactivated catalyst should have significant bearing on the formulation of models for ion exchange resin catalysis of aqueous reactions and on the performance of commercial sucrose inversion reactors, which may be subject to catalyst deactivation by feed stream impurities.

The approach followed in this work was to carry out fixed bed inversion studies under steady state conditions with a variety of catalysts deactivated by partial replacement of hydrogen ions by noncatalytic cations. As will be shown, the results of such experiments indicate that first-order behavior is maintained throughout. Lowering of catalyst activity is directly related to hydrogen ion content of the resin but also depends on the specific deactivating ion used.

EXPERIMENTAL

The experiments were carried out in a water jacketed Pyrex reactor with a diameter of 1 in. The reactor and related flow equipment were the same as used previously by Lifshutz and are described in detail elsewhere (*3* to *5*). All experiments were made at a temperature of 60°C.

The resin used as catalyst was Dowex 50W-X8. It was carefully sized by wet sieving in the sodium form to obtain a 20 to 25 mesh (U.S. Standard) fraction having an average diameter of about 0.8 mm. in the hydrogen form. The packed volume of resin within the reactor was 50.0 ml.

The resin was completely acidified at the beginning of this work by contact in a packed bed with a large excess of aqueous hydrochloric acid; 50.0 ml. of this acidified resin was loaded into the reactor and maintained in place thereafter. The deactivation or poisoning of the catalyst was accomplished in place by contacting the packed bed with a tenfold excess of prepared solution containing hydrochloric acid and either sodium chloride or potassium chloride in desired ratios. Slow passage of these solutions through the bed, followed by a thorough washing with deionized water, was deemed sufficient to produce a resin phase of uniform composition within each resin particle and throughout the packed bed.

The hydrogen ion content (acid capacity) of fully acidified resin was measured by titration of the acid solution produced by washing the resin with excess sodium chloride solution. The capacity of deactivated catalyst was similarly measured on a small sample of resin which was treated with deactivating solution in exactly the same way as that resin within the packed bed.

The sucrose feed solutions were prepared with reagent grade sucrose and deionized water and maintained at a concentration of 15 wt. % sucrose. Analysis of the feed and reacted solutions was by the usual polarimetric techniques (*5*).

RESULTS AND DISCUSSION

The irreversible sucrose inversion reaction is as follows:

$$\begin{array}{llll} C_{12}H_{22}O_{11} & + H_2O \xrightarrow{H+} C_6H_{12}O_6 & + C_6H_{12}O_6 & \\ (+)\text{-Sucrose} & \qquad (+)\text{-Glucose} & (-)\text{-Fructose} & (1) \end{array}$$

On the assumption of first-order kinetics, the fractional conversion of sucrose should be related to apparent space time (based on completely acidified resin volume) by the usual plug flow reactor equation:

$$\ln(1 - x) = -K\tau_a \qquad (2)$$

It is expected, of course, that the rate constant K will be a function of the hydrogen content (capacity) of the resin.

The results of some of the experiments made with sodium poisoned catalyst and potassium poisoned catalyst are shown in the first-order plots of Figures 1 and 2, respectively. It is clear from these data that the first-order behavior is maintained as the catalyst activity decreases.

The dependence of K on resin capacity is more clearly indicated in the logarithmic plot of Figure 3. The data can be well represented by straight lines over large ranges on these plots, and appropriate lines and equations are

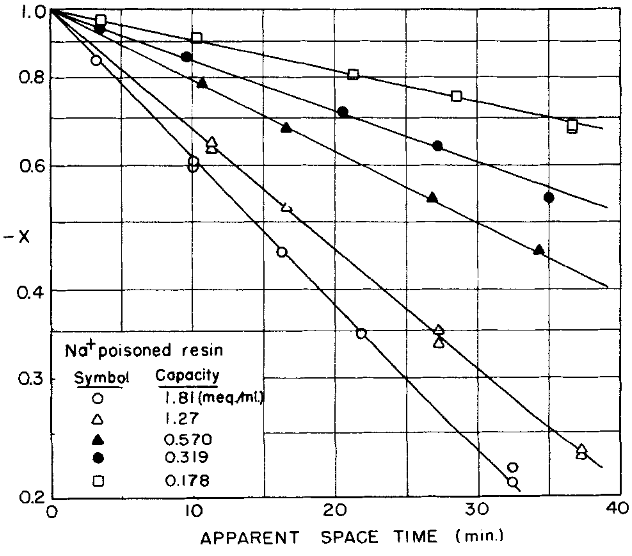

Fig. 1. First-order plot for sodium poisoned catalyst.

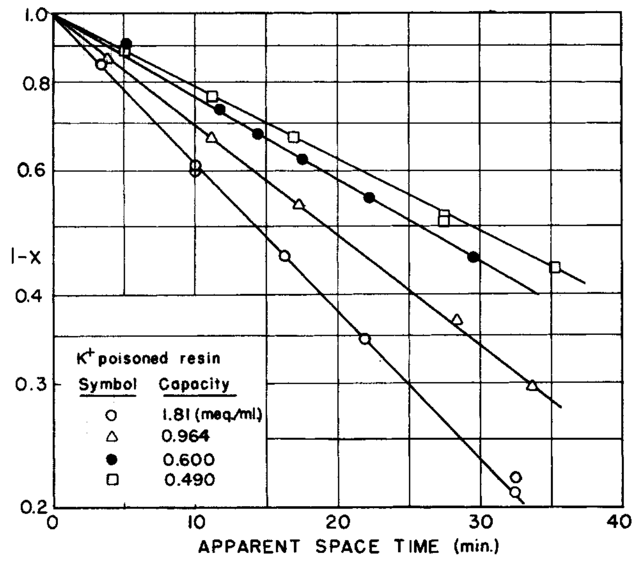

Fig. 2. First-order plot for potassium poisoned catalyst.

also indicated on the figure.

At this point a question arises concerning the form of the dependence shown on Figure 3 as well as the apparent difference in the effects of sodium and potassium ions. Explanations of these effects are to be found in an analysis of the basic rate processes at work in the inversion reaction.

As indicated earlier, the inversion reaction within fully acidified spherical ion exchange beads is strongly influenced by intraparticle diffusion of sucrose. If it is assumed that even for partially deactivated catalysts the distribution of H^+ ions within the particles is uniform, then the steady state rate of reaction per unit volume of resin will be related to sucrose concentration at the particle surface as follows:

$$R_s = E\,k\,\lambda\,C_s \tag{3}$$

The effectiveness factor E is the usual Wheeler-Thiele parameter (6) given by

$$E = \frac{3}{h^2}\left[h \coth(h) - 1\right] \tag{4}$$

where

$$h = R\sqrt{\frac{k}{D_s}} \tag{5}$$

Now, as another reasonable assumption, the first-order rate constant k of Equation (3) may be taken to be directly proportional to the concentraion of the H^+ ions within the catalyst:

$$k = k_0 \overline{C}_H \tag{6}$$

If Equations (3) and (6) are then combined with the usual packed bed material balance, one may write

$$\ln(1-x) = -k_0 \overline{C}_H \lambda (1-\epsilon) E \tau \tag{7}$$

Comparison of this result with Equation (2) is facilitated by replacing E by its asymptotic forms. Thus, since

$$E = \begin{cases} 3/h & \text{for large } h \\ 1.0 & \text{for small } h \end{cases} \tag{8}$$

we may rewrite Equation (7) with the help of Equations (5) and (6) as follows:

$$\ln(1-x) = \begin{cases} -\dfrac{3\lambda(1-\epsilon)}{R}\sqrt{k_0 \overline{C}_H D_s}\,\tau & \text{for large } h \\ -k_0 \overline{C}_H \lambda (1-\epsilon)\tau & \text{for small } h \end{cases} \tag{9}$$

Before these forms are compared with the experimental data, it is well to consider the effect of resin particle size changes. It is well known that ion exchange particles shrink when the hydrogen ions are replaced by sodium or potassium ions, the shrinkage amounting to about 10% of the original volume for complete exchange. This may be taken into account by defining a particle volume ratio f and apparent space time and capacity (based on completely acidified resin volumes) as follows:

$$f(\overline{C}_H) = \frac{V}{V_a} \tag{10}$$

$$\tau_a = \frac{V_a}{Q} = \frac{\tau}{f} \tag{11}$$

$$\overline{C}_{Ha} = \overline{C}_H \frac{V}{V_a} = \overline{C}_H f \tag{12}$$

$$R = f^{1/3} R_a \tag{13}$$

Insertion of these relations into Equation (9) yields

$$\ln(1-x) = \begin{cases} \dfrac{-3\lambda(1-\epsilon)}{R_a}\sqrt{k_0 \overline{C}_{Ha} D_s}\,\tau_a f^{1/6} & \text{for large } h \\ -k_0 \overline{C}_{Ha} \lambda (1-\epsilon)\tau_a & \text{for small } h \end{cases} \tag{14}$$

However, since $f(\overline{C}_H = 0) \approx 0.9$, it can be seen that the effect of particle shrinkage will be essentially negligible.

Thus, we may finally expect the apparent first-order rate constant to have the following asymptotic forms:

$$K = \begin{cases} \dfrac{3\lambda(1-\epsilon)}{R_a}\sqrt{k_0 \overline{C}_{Ha} D_s} & \text{for large } h \\ k_0 \lambda (1-\epsilon)\overline{C}_{Ha} & \text{for small } h \end{cases} \tag{15}$$

Equation (15) predicts that K will be proportional to $(\overline{C}_{Ha})^{1/2}$ for large h and $\overline{C}_{Ha}$ for small h. Recalling the definitions of h from Equation (5), we might expect the square-root dependence for large $\overline{C}_{Ha}$ and the first-power dependence for small $\overline{C}_{Ha}$. The data for K^+ poisoning seem in excellent agreement with the former limit but clearly do not extend to sufficiently low values of $\overline{C}_{Ha}$ for the second asymptote to appear. The Na^+ data do show some evidence of a higher slope on Figure 3 as $\overline{C}_{Ha}$ decreases below about 0.3 meq./ml. On the other hand, the remaining sodium data clearly do not conform to the square-root dependence predicted.

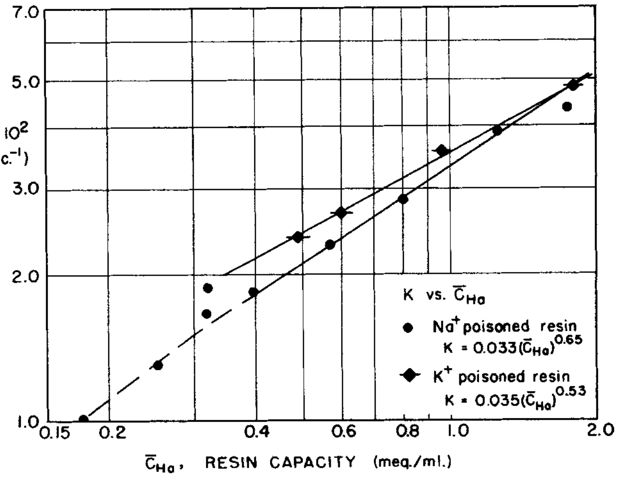

Fig. 3. Catalyst activity vs. acid content.

However, this might be explained by variations in the sorption coefficient λ and the intraparticle diffusivity of sucrose as the resin composition changes. In fact, O'Connell (*2*) has reported that D_s for completely acidified resin is 1.15 times larger than for sodium form resin, while λ is 1.30 times higher in acid form resin. In the absence of intermediate data, one may assume that λ and D_s then vary linearly with $\overline{C}_{Ha}$ between these limits. If such a variation is arbitrarily forced into a form such that $\lambda(D_s)^{1/2}$ is proportional to $\overline{C}_{Ha}$ raised to an arbitrary power, it may be shown that a good fit results when this power is 0.17. When this is then put back into the large h asymptote of Equation (15), one sees that K should vary with $\overline{C}_{Ha}$ to the 0.67 power. This is now in excellent agreement with the experimental results of Figure 3.

Finally, one may question the use of different arguments for the Na^+ and K^+ cases. Support for this approach may be found in the higher free water content of K^+ loaded resins. As pointed out by Helfferich (*7*), diffusion of nonelectrolytes is higher in the K^+ form than in the Na^+ form, although the total water contents of both forms are comparable. Similar behavior with respect to the sorption coefficient is likely. Therefore, the differences in the results are not altogether surprising. In fact, recent data obtained by Handel (*8*) with Ca^{++} poisoned resin show good linearity on a plot similar to Figure 3 but a dependence on $\overline{C}_{Ha}$ to the 0.83 power. Since the free water content of Ca^{++} resin is still lower than Na^+ form resin, the larger power is perhaps not unexpected.

The net result of this work has been the demonstration that the inversion of sucrose by acidified ion exchange resin catalyst remains of apparent first order as catalyst activity falls. The change in activity has been shown to be directly related to the apparent acid capacity of the resin catalyst. Analysis of the process has shown that the dependence may be predicted quantitatively in terms of the usual Wheeler-Thiele formulation for reaction coupled with intraparticle diffusion but with due regard for the effects of catalyst composition on the diffusivity and sorption coefficient of sucrose in the resin. It is clear that the analysis shown here is qualitatively correct and can be made quantitative if sufficient supporting data are available for the deactivating ions in question.

NOTATION

C_s = concentration of sucrose in solution, moles/liter
$\overline{C}_H$ = concentration of hydrogen ions in resin, meq./ml.
D_s = diffusivity of sucrose within resin, sq.cm./sec.
E = effectiveness factor
f = ratio of resin volume to completely acidified volume
h = Thiele modulus, see Equation (5)
k = first-order rate constant, sec.$^{-1}$
k_0 = second-order rate constant for sucrose inversion, ml./(sec.)(meq.)
Q = volumetric flow rate, liters/min.
R = resin particle radius, cm.
R_s = rate of inversion per unit resin volume, moles/(cc.)(sec.)
V = resin volume, cc.
x = fractional conversion of sucrose

ϵ = void fraction in packed bed reactor
λ = sorption coefficient for sucrose
τ = reactor space time, min.

Subscript

a = apparent, based on resin in the completely acidified form

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Motion of Liquid Drops in Non-Newtonian Systems

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Predictive equations for terminal velocities of liquid drops in Newtonian and non-Newtonian systems are reviewed. The wave theory analogy is extended to include liquid-liquid systems. Experimental data obtained with seven different systems are presented. The agreement with predictive equations is satisfactory. Interface rigidity was observed in all the systems investigated.

While the motion of gas bubbles through non-Newtonian liquids has been studied both theoretically and experimentally (*1* to *3*, *11*), much less is known about the analogous problem for liquid drops (*4*, *11*); as far as we know, no information at all is available concerning the motion

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