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DIFFUSION OF CARBOHYDRATES IN ANION EXCHANGERS

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ABSTRACT

Selectivity problems may arise for the isomerization of sugars catalysed by ion-exchangers if diffusion becomes relatively slow. Therefore, experiments were carried out to determine the diffusion coefficients of glucose in a gel type (IRA 401) and a macroreticular type (IRA 938) of ion exchanger. Formulae are given that correlate diffusivity with sugar concentration, temperature and polymer fraction of the ion-exchanger.

INTRODUCTION

For the isomerization of glucose to fructose with these catalysts, the glucose has to diffuse into the anion exchanger before it can be adsorbed [5] as glucose anion. This will isomerize to the fructose anion [6-8] and, the fructose will in his turn have to diffuse out of the ion exchanger. As the activation energy for diffusion is generally lower than for the chemical reaction, we can expect a diffusion limitation at higher temperatures.

As the degradation rate of the fructose anion is about three times as high as that of the glucose anion, this will lead to a decrease of the selectivity. For this reason it is very important to take the diffusion processes inside the ion exchangers into account, when studying the kinetics of chemical reactions catalysed by resins.

Diffusion in homogeneous solution

We have reported in a preceding article [5] that the glucose anion concentrations inside the ion exchangers are relatively high. Gladden and Dale [9] found that at high concentrations the diffusion coefficient decreases, while its activation energy increases. In Table 1 some of their data are given. These data will be applied for the development of an overall equation for diffusion. For that purpose the data are replaced by the following expressions:

\[
D_G^{298} = D_G^{298(0)} e^{-5.7 \times 10^{-5} G} \quad \text{with} \quad D_G^{298(0)} = 0.675 \times 10^9 \text{ m}^2 \text{s}^{-1}
\]  

(1)
\[ E_{\text{diff}} - E_{\text{diff},G} = 0 \left( 1 + 6.4 x_G \right) \quad \text{with} \quad E_{\text{diff},G} = 17.6 \text{ kJ mol}^{-1} \]  

(2)

\[ x_G = \frac{M_{\text{H}_2\text{O}} C_G}{c_G - (M_G - M_{\text{H}_2\text{O}}) C_G} \]  

(3)

**TABLE 1**

Concentration dependency of the diffusion rate and the activation energy for diffusion of glucose in solution.

| \(C_G [\text{mol m}^{-3}]\) | 0  | 580  | 1170 | 2620 | 4330 |
| \(D_G \cdot 10^9 [\text{m}^2 \text{s}^{-1}]\) | 0.675 | 0.580 | 0.486 | 0.302 | 0.133 |
| \(E_{\text{diff}} [\text{kJ mol}^{-1}]\) | 17.6 | - | - | 24.7 | 32.7 |

**Diffusion in ion exchangers**

A number of ways to describe diffusion in ion exchangers have been proposed:

- **As molecular diffusion:**
  Boyd et al. [10] and Reichenberg [11] suppose that the undisassociated molecule diffuses into and through the ion exchanger until an active site \((R-\text{NR}_4^+\text{OH})\) has been reached and adsorption takes place. For a sugar:

  \[
  \text{SH}_{\text{sol}} \rightleftharpoons \text{SH}_{\text{ie}} \]  

  \[
  \text{SH}_{\text{ie}} + R-\text{NR}_3^+\text{OH}^- \rightleftharpoons R-\text{NR}_3^+\text{S}^- + \text{H}_2\text{O}_{\text{ie}} \]  

  (4)

  (5)

  The counter ions are considered to be more or less static and bound on the active sites. No interaction of the diffusive particles with the exchanger material is supposed and no backflow of expelled water is taken into account. A method is given to calculate \(D_{\text{G},\text{ie}}\) from diffusion experiments.

- **As ionic diffusion:**
  Helfferich and Plesset [12-14], Marinsky [15] and Turner et al. [16] consider the distribution of the counter ions to be dynamic. These ions are mobile and are interchangeable with other counter ions. When molecular sugar adsorbs, ionization takes place immediately at the surface of the particle and the sugar ion diffuses into the particle. To maintain electro-neutrality, \(\text{OH}_{\text{ie}}^-\) is transported in the opposite direction with the same flux. The diffusion of \(S_{\text{ie}}^-\) is directly related to the diffusion of \(\text{OH}_{\text{ie}}^-\). Helfferich gives a method to calculate \(D_{S^-}\) from experimental results when \(D_{\text{OH}_{\text{ie}}^-}\) is known.

From our study of the adsorption of sugars in resins [5] we conclude that depending on the concentration in the bulk, a combination of molecular and ionic diffusion can take place. As \(D_{\text{OH}_{\text{ie}}^-}\) in highly concentrated sugar solutions were not available in the literature, we decided to apply the model of Boyd on our experimental data. In the discussion we will return to this matter.
With the Boyd model we can derive from the experimental data a value for $D_{S_{ie}}$. For an estimate of the diffusion constant as a function of the properties of solution and ion exchanger, four types of relations are known [17-20]. Of these, the relations of Zimmerman [17] and of Katoaka et al. [18] will not be discussed because they have little practical value. Mackie and Meares [19] give for the diffusion coefficient in the resin:

$$D_{S_{ie}} = D_S \frac{(1 - x''_{pol})/(1 + x''_{pol})^2}{(1 - x''_{pol})/(1 + x''_{pol})}$$ \hspace{1cm} (6)

with $x''_{pol}$ being the polymeric fraction, as we have discussed earlier [28]. In their model the ion exchanger is considered to be a concentrated polyelectrolyte solution.

Yasuda et al. [20] have developed the relation:

$$D_{S_{ie}} = D_S \exp\left(-\frac{Y_{AS} \cdot x''_{pol}}{1 - x''_{pol}}\right)$$ \hspace{1cm} (7)

with $Y_{AS}$ = constant of Yasuda.

The constant of Yasuda depends on the type of material diffusing into the exchanger. This derivation is based on Cohen's free volume theory [21,22] and on Doolittle's observation [23,24] that for a comparable constant (for viscosity) a relation exists that, translated into terms of Yasuda's constant, reads:

$$Y_{AS} = \frac{Y_{AS0}}{E_{diff}/E_{diff,S=0}}$$ \hspace{1cm} (8)

On the basis of Doolittle's study it can further be assumed that $Y_{AS}$ is independent of the type of exchanger and the temperature. Fernandez-Prini and Philipp [25] extended the model of Yasuda in writing:

$$D_{S_{ie}} = Q \cdot D_S \exp\left(-\frac{Y_{AS} \cdot x''_{pol}}{1 - x''_{pol}}\right)$$ \hspace{1cm} (9)

where $Q$ is a correction factor for the electrostatic interaction between the ions and the ion exchanger.

We have been unable to find literature data for the diffusion of sugars in basic ion exchange resins. Lagos and Kitchener [26] measured $D_G$ and Wong et al. [27] measured $D_F$ in acidic cation resin. The model of Yasuda gave the best description of their experimental data with

$$Y_{AS0} = Y_{AS,F=0} = 1.0 \text{ at low } C_{S_{ie}} \text{ (at low } C_{S_{ie}} \text{)}$$ \hspace{1cm} (10)

and

$$Q \approx 1.0 \text{ (electrostatic interaction is negligible)}$$ \hspace{1cm} (11)
For the diffusion of glucose or fructose in anion exchangers the constant of Yasuda must have the same value because it is independent of the resin. The influence of the electrostatic interaction (Q), however, is not known in the anion exchangers. We will return to this matter when the experimental results are discussed.

![Diagram of diffusion experiments](image)

**FIGURE 1** Block diagram for diffusion experiments.

**EXPERIMENTAL**

The diffusion experiments have been carried out under N\textsubscript{2} in a thermostatted (298 K) stirred reactor of 200 cm\textsuperscript{3}. A glucose solution (100 cm\textsuperscript{3}, 1 M) was pumped through the measuring cell and the reference cell of a thermostatted refraction meter (Waters, R4). When the baseline was stable, the reference cell was short-circuited and about 1 meq of filtered exchanger in the hydroxyl form was brought into the reactor. Diffusion of glucose into the exchanger caused a decrease of the concentration in the solution, which resulted in a change of the refraction index. In Figure 1 a block diagram is given. With the aid of a calibration curve for the refractive index, the change of the glucose concentration with time was measured, yielding the rate of glucose adsorption.

**RESULTS AND DISCUSSION**

When studying the diffusion of glucose inside the anion exchanger, it is important to be sure that the diffusion in the bulk of the liquid has no influence on the outcome of the experiments. As no influence could be found when the stirring rate was increased more than threefold, we conclude that no bulk diffusion limitation occurs.

From the concentration decrease in the solution during the experiment the degree of coverage of the exchanger (\(\theta_e\)) can be calculated.

The diffusion coefficient in the exchanger (\(D_e\)) can then be calculated according to the method of Boyd et al. [10] and Reichenberg [11].
FIGURE 2 Diffusion coefficient of glucose in IRA 401 (D_{Gie}) as a function of the internal concentration (C_{Gie}). The different type of points correspond to different experiments.

For \( \theta_G,t/\theta_G,t^\infty < 0.85 \):

\[
D_{Gie}^t = d_p^2/(4\pi^2) \cdot d/dt \left[ 2\pi - \pi^2 \cdot \theta_G,t/\theta_G,t^\infty/3 - 2\pi \cdot \sqrt{1 - \pi \cdot \theta_G,t/\theta_G,t^\infty/3} \right]
\]

(12)

For \( \theta_G,t/\theta_G,t^\infty > 0.85 \):

\[
D_{Gie}^t = d_p^2/(4\pi^2) \cdot d/dt \left[ -\ln(\pi^2/6 \cdot (1 - \theta_G,t/\theta_G,t^\infty)) \right]
\]

(13)

with \( \theta_G,t \) = coverage of the resin with glucose at a time \( t \);

\( \theta_G,t^\infty \) = coverage of the resin with glucose at equilibrium;

\( d_p \) = particle diameter, being a function of the coverage (see reference 28).

Due to the rather low reproducibility the experiments have been carried out in a quadruplicate (IRA 401) and in triplicate (IRA 938). From the degree of coverage of the exchanger and its pore volume the internal concentrations during the experiment can be calculated. The diffusion coefficients calculated from the experimental data are plotted as a function of the internal concentration in Figures 2 (gel-type resin IRA 401) and 3 (macroreticular-type IRA 938).
FIGURE 3 Diffusion coefficient of glucose in IRA 938 ($D_{Gie}$) as a function of the internal concentration ($C_{Gie}$).

In the figures, our results are compared with the diffusion coefficients in pure solutions calculated according to Gladden and Dole (equation 1) and in resins according to Yasuda et al. (equation 7) and Mackie and Meares (equation 6). In spite of the spread in our experimental data it is plausible that also the diffusion of sugars in different types of anion exchangers can be approximated with the diffusion coefficient, based on the relation of Yasuda [20], as given in equation 7.

For monosaccharides, and perhaps even for disaccharides, it is plausible that the concentration dependence of the diffusion (relation 1) and of the activation energy for diffusion (relation 2) will be the same for all types of sugar.

The relations (14) and (15) are then valid for all types of sugars and resins as a function of the temperature ($T$) and the internal concentration ($x_{Si,e}$). The influence of the type of sugar is expressed in $D_{S=0}$ and $E_{diff,S=0}$. The resin characteristics are represented in the polymeric fraction $x_{pol}^n$. For hexoses the best value of $Y_{S=0} = 1.0$.

LIST OF SYMBOLS

LATIN SYMBOLS

$C_i$ concentration $\text{mol m}^{-3}$
$D_i$ diffusion coefficient $\text{m}^2 \text{s}^{-1}$
$d$ diameter $\text{m}$
\[ E \quad \text{activation energy} \quad \text{kJ mol}^{-1} \]

\[ G \quad \text{glucose} \]

\[ M_i \quad \text{molweight of component } i \quad \text{kg mol}^{-1} \]

\[ Q \quad \text{electrostatic interaction factor} \]

\[ R \quad \text{gas constant (8.315)} \quad \text{J mol}^{-1} \text{K}^{-1} \]

\[ S \quad \text{sugar (} S = \text{SH} + \text{S}^- \text{)} \]

\[ S^- \quad \text{ionized sugar} \]

\[ SH \quad \text{molecular sugar} \]

\[ T \quad \text{temperature} \quad \text{K} \]

\[ X \quad \text{mol fraction} \]

\[ x' \quad \text{volume fraction} \]

\[ \chi_A \quad \text{constant of Yasuda for sugar } S \]

**GREEK SYMBOLS**

\[ \upsilon_i \quad \text{coverage of component } i \quad \text{mol eq}^{-1} \]

\[ \rho \quad \text{liquid density} \quad \text{kg m}^{-3} \]

**SUBSCRIPTS**

\[ \text{diff} \quad \text{diffusion} \]

\[ i \quad \text{component} \]

\[ \text{ie} \quad \text{ion exchange resin} \]

\[ p \quad \text{particle (= pore + polymer)} \]

\[ \text{pol} \quad \text{polymer (= particle - pore)} \]

\[ S = 0 \quad \text{infinitely diluted sugar solution of } S \text{ in water} \]

\[ \text{sol} \quad \text{solution in the bulk} \]

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