

REACTION AND DIFFUSION ON AMBERLYST-15 ION-EXCHANGE POLYMER

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Abstract: In this work, the effects of liquid polarity on the intrapolymer diffusion rates of iso-Butene, using the heterogeneously catalysed hydration of i-Butene to tert-Butyl alcohol, are studied. Values for the effective diffusivity are correlated as a function of tert-Butanol concentration and temperature. The tortuosity factor of the solid polymer matrix is seen to decrease with temperature and increase with alcohol content. Tentative conclusions regarding the shrinkage of the macroporous matrix, are drawn.

INTRODUCTION

The purpose of the present communication is to study the effect of liquid polarity on the diffusion rates of iso-Butene (iB) within the liquid-filled pores of Amberlyst-15 (A-15) polymer. To this end, reaction rates for iB hydration in the presence of different concentrations of product, tert-Butyl alcohol (TBA), were measured under varying conditions (temperature, 303 to 333 K; A-15 particle size, from 0.51 to 1.07 mm; and TBA concentrations, from 0.1 to 2.5 kmol/m³). Measurements were made with small concentrations of iB, in the range of 10⁻² kmol/m³, such that aqueous solutions saturated with iB were homogeneous.

POLYMER PROPERTIES

A-15 is a styrene-divinylbenzene crosslinked copolymer in which the catalytic active groups have been introduced by sulphonation after polymerization. The active groups account for 4.7 eq/kg. The polymer particles are spherical beads composed by agglomerates of gel-type microspheres (about 30 nm in size) surrounded by a macroporous matrix (Refs. 1, 2). Further information from the supplier (Rohm & Haas, Barcelona), suggests that only 5% of the active sites are in the pore wall surface, while the remaining 95% are burried in the gel structure. Pore-volume distribution for the dry polymer is represented in Fig. 1, in terms of the pore-volume vs. pore diameter (Ref. 3). The total porosity is 35% with an average diameter of 26 nm. About 75% of the pore volume is in the pores smaller than 30 nm,

hence corresponding to the microparticle porosity. Because of the small size of the microparticles (with Thiele modulus of 10^{-3}) the reaction is unlikely to be retarded by diffusion in the microspheres. Thus, the measured diffusivities correspond to the macropore volume.

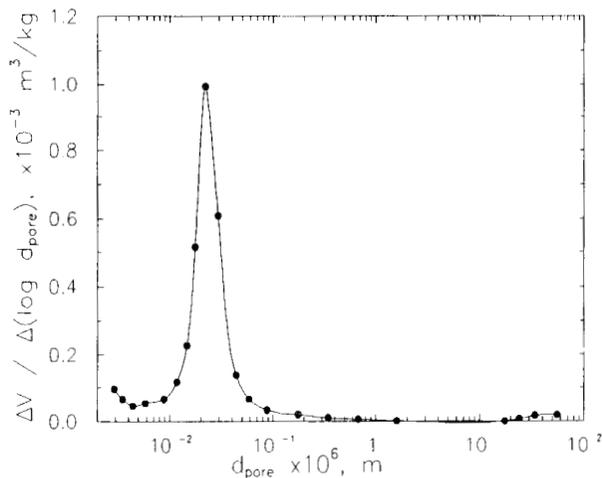


Fig. 1. Pore-volume distribution of dry A-15 polymer (Ref. 3)

EXPERIMENTAL METHOD

Full details regarding the experimental setup and methodology are given elsewhere (Ref. 4). Suffice it to recall here that hydration of iB was performed in a liquid-full, packed-bed reactor, whose liquid feed was continuously batch-recycled to a reservoir with a pump. An initially iB-saturated aqueous solution was continuously passed through the bed of A-15, and returned to the reservoir. Gas-chromatographic analysis of the remaining iB in the reservoir as a function of time, provides values of the instantaneous hydration rates. High liquid flowrates and a small mass of catalyst, insured differential operation (per pass conversions less than 10-15 %).

DIFFUSION WITH REACTION WITHIN POLYMER PORES

For the batch-recycle reaction runs, an expression for the concentration of iB remaining in the reservoir liquid is derived. The conservation equations for iB in the pores of the A-15 spheres and in the recycle liquid, respectively, are:

$$D_e \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] = \rho r_B + \varepsilon \frac{\partial C}{\partial t} \quad (1)$$

$$\frac{3}{\rho R} \left[-D_e \frac{\partial C}{\partial r} \right]_{r=R} = V \frac{dC_L}{dt} \quad (2)$$

with the initial and boundary conditions:

$$C(t=0, r > 0) = 0 \quad (3)$$

$$C_L(t=0) = C_{L0}$$

$$C(t > 0, r=R) = C_L(t)$$

$$\left(\frac{\partial C}{\partial r} \right)_{t > 0, r=0} = 0$$

In eq. (1), the following kinetic expression for r_B is available from a previous work (Ref. 5). This is:

$$r_B = \frac{k (C C_W - C_a/K)}{1 + K_a C_a} \quad (4)$$

where the kinetic, inhibition and equilibrium constants, as a function of temperature are available (Ref. 5). Velo showed (Ref. 4) that an analytical solution to the above system of equations (1)-(2), subject to (3), is possible. In terms of the reduced time, θ , this is:

$$\frac{C_L(\theta)}{C_{L0}} = \frac{C_{eq}}{C_{L0}} + \sum_{n=1}^{\infty} \frac{\left[1 - \frac{\phi^2 X_e}{u_n^2} \right] \exp \left[(u_n^2 - \phi^2) \frac{\theta}{\alpha} \right]}{1 + \frac{3\alpha}{2} \left[\frac{\coth(3u_n)}{3u_n} - \coth^2(3u_n) + 1 \right]} \quad (5)$$

where the series accounts for the dynamic period before chemical equilibrium is reached. The summation is carried over the successive roots of the transcendental equation:

$$3(u_n^2 - \phi^2) + \alpha [3u_n \coth(3u_n) - 1] = 0 \quad (6)$$

where θ , ϕ , X_e and C_{eq} and α , are defined in the Nomenclature. Note that in the governing equations, the intra-polymer diffusivity, D_e , is the only adjustable parameter, since all other parameters are known either from geometry and experimental conditions or from measurement. Therefore, performing several reaction runs at different TBA concentrations,

it is possible to determine the corresponding diffusivities from the time-domain curve-fitting of the experimental iB concentration data, to the calculated solution, eq. (5), at all times. Typical results are shown in Fig. 2, where dashed lines represent the calculated responses using the diffusivities of iB in pure water. As seen, the curves can be used to get reasonable estimates of diffusivity under different conditions. The calculated values using the above curve-fitting method are given in Tab. 1, as a function of C_a and T for the two sizes of polymer particles used. The diffusivities can be well correlated with the following empirical equation:

$$D_e = \exp(-9.52 - 0.551 C_a - 3690/T) \quad (7)$$

for the ranges of TBA concentration and temperature of this study.

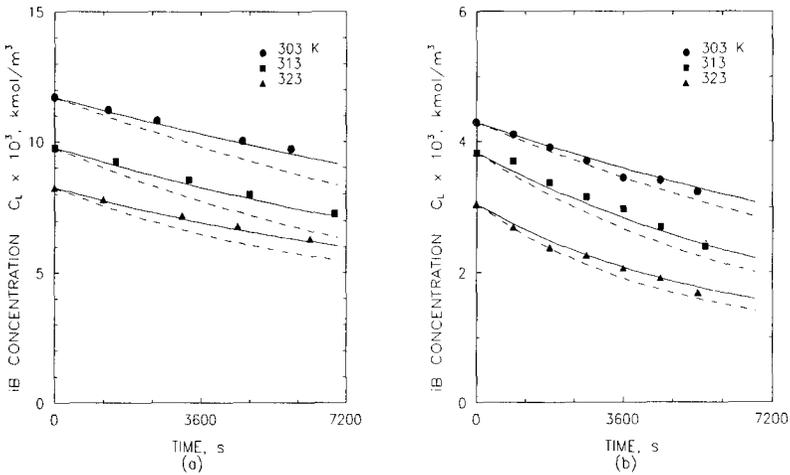


Fig. 2 Sensitivity of reaction rates to values of effective diffusivity of iso-Butene. a) $C_a = 2.5 \text{ kmol/m}^3$, b) $C_a = 1.0 \text{ kmol/m}^3$

DISCUSSION AND FINAL REMARKS

From the dependence of diffusivity on temperature (Tab. 1) it seems clear that the pore surface migration as a transport mechanism can be ruled out. Defining the tortuosity factor of the pore structure as (Ref. 6):

$$\tau = \frac{D \varepsilon}{D_e} \quad (8)$$

and using estimated values of the molecular diffusivity in the mixed solvent, the fitted D_e

values (Tab. 1) can be used to estimate the polymer tortuosity factor, provided that the porosity is constant (that of the dry polymer, $\varepsilon = 0.36$).

Tab. 1 Iso-Butene effective diffusivities.

d_p , mm	0.51			1.07			
C_a , kmol/m ³	0	0.09	2.45	0.1	0.48	0.95	2.05
T, K	$10^{10} D_e$, m ² /s						
303	3.7	1.7	0.7	1.8	2.6	2.7	1.1
313	5.1	4.5	1.2	4.0	3.3	3.5	1.5
323	8.0	5.1	1.7	5.1	6.2	5.2	2.8
333	11.	7.3	2.4	5.8		9.1	

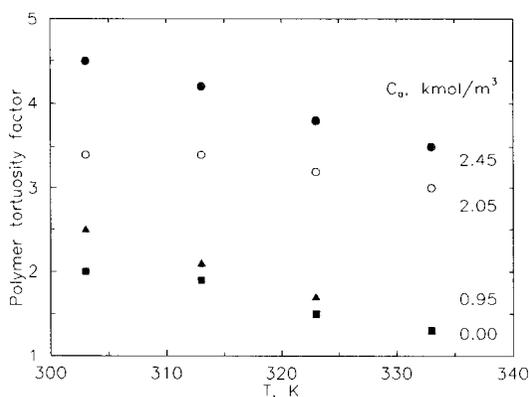


Fig. 3 Apparent tortuosity factor of A-15 as a function of temperature, at constant C_a .

The results of this calculation appear in Fig. 3. As is observed, tortuosity factors increase largely with TBA concentration (to the accepted value of about 4), and decrease slightly with T. This could be due to either pore shrinkage under liquid media of different polarity, or due to some slowdown in rate, because of a decrease in a transport coefficient. In fact, Velo *et al.* (Ref. 7) found that the kinematic viscosities of aqueous TBA, decreased largely with increasing TBA concentration. On the other hand, pore shrinkage may affect the internal porosity of the particles, so that ε decreases in eq. (8). This is a rather plausible cause that should be studied further. In a previous publication (Ref.5) we found that there was an

intrinsic decrease in reaction rate, caused by high TBA concentrations. Additional independent measurements on the swelling of the polymer matrix, and how this affects the pore structure, are needed.

NOMENCLATURE

C, C_a	Intra-polymer iso-Butene and TBA concentrations, kmol/m^3
C_L	Iso-Butene liquid-phase concentration, kmol/m^3
D, D_e	Molecular and effective diffusivities, m^2/s
K_a	Product inhibition constant, m^3/kmol
K	Chemical Equilibrium constant, m^3/kmol
k	2nd-order kinetic constant, $\text{m}^6/(\text{kg cat} \cdot \text{s} \cdot \text{kmol})$
k_1	Pseudo-1st order kinetic constant, $k_1 = k C_w / (1 + K_a C_a)$, $\text{m}^3/(\text{kg cat} \cdot \text{s})$
m	Mass of dry A-15, kg
R	Radius of spherical particle, m
r_B	Reaction rate, $\text{kmol iB}/(\text{kg cat} \cdot \text{s})$
r	Radial coordinate, m
T	Temperature, K
t	Time, s
V	Liquid volume, m^3
X_e	Equilibrium ratio, C_{eq}/C_{L0} , eq. (5)
α	Ratio pore-to-liquid volumes, $m \varepsilon/(\rho V)$
ε	Polymer internal void fraction
ϕ	Thiele modulus, first-order reaction, $\phi = (R/3) (\rho k_1 / D_e)^{1/2}$
ρ	Particle density, kg/m^3
τ	Polymer tortuosity factor
θ	Dimensionless time, $\theta = m k_1 t/(\phi^2 V)$

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