Kinetics of the Sulfonation of Macroporous Poly(styrene-co-divinylbenzene) microparticles

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Macroporous cation-exchange resins can be synthesized by sulfonation of poly(styrene-co-divinylbenzene) microparticles. The degree of sulfonation attained, and hence their cation-exchange capacity, depends on factors related to the polymerization process, such as the percentage divinylbenzene (%DVB) and of the monomeric fraction added to the polymerization mixture (Fm), as well as on variables related to the sulfonation process itself, such as temperature and time of sulfonation. Mass transfer of the sulfonation agent by diffusion inside the microparticles is governed by different diffusion mechanisms due to the existence of gel-type nanoparticles and pores of very different sizes inside them. Detailed modeling of these processes is difficult, but the use of simplified models addressing the diffusion of a liquid into a spherical solid seems to be suitable for the process to be described. Thus, in the present work experiments aimed at determining the sulfonation kinetics of polymeric microparticles were performed. After attempting to fit some of the most widely used models to our experimental results, it was found that a polynomial model used to study the kinetics of ion-exchange processes is also useful to explain the kinetics of the sulfonation process.

1. Introduction

Macroporous cation-exchange resins are employed in many fields, their use ranging from the separation of the components of a mixture to their use in the field of catalysis. The synthesis of this type of resin can be carried out by sulfonation of poly(styrene-co-divinylbenzene) (poly(ST-co-DVB) microparticles with hot sulfuric acid (Toro, 2008). The degree of sulfonation achieved depends on variables related to the polymerization process, such as the percentage of divinylbenzene (%DVB) (which affects the degree of cross-linking) and of the monomeric fraction added to the polymerization mixture (Fm) (which has an important influence on the size of the pores), as well as on the temperature and time of sulfonation.

In batch processes, the sulfonation agent surrounds the porous microparticles and sulfonation commences at their external surface. The next step involves the diffusion of the acid through the pores, which is governed by different diffusion mechanisms owing to the existence of gel-type nanoparticles and pores of very different sizes inside the microparticles. Detailed modeling of these processes would be unpractical owing to the

need of a large number of parameters and the considerable computational effort required to find their solution. Thus, in the scientific literature it is usual to find simplified models addressing the diffusion of a liquid into a solid particle that readily allow analytical solutions to be found. However, despite the industrial and economic relevance of the manufacture of cation-exchange resins there is a lack of studies dealing with the sulfonation kinetics of polymeric microparticles. Accordingly, the present work aims at offering a contribution to this field through study of the sulfonation kinetics of polymeric microparticles with different structural characteristics. Our objective was to find a model of the sulfonation process that will permit the design of experimental procedures oriented towards the preparation of cation exchange resins with predetermined degrees of sulfonation and porosities.

2. Experimental

2.1 Characteristics of the polymeric beads
In order to obtain microparticles with different types of porosity, the polymeric beads were synthesized with several degrees of cross-linking (% DVB) and different proportions of porogen agent (n-heptane). The monomeric fraction, Fm, is the proportion of monomers in the reaction mixture. The values used in the synthesis and the characteristics of the product, such as specific surface area and micro-, meso- and macropore volume, are given in Table 1.

Table 1. Experimental conditions used in the synthesis of the macroporous polymeric beads

Resin number	%DVB	F_m	Structural characteristics[a]				r_p (cm)	q_m (meq/g)
			S_{BET} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_{macro} ($cm^3\ g^{-1}$)		
1	25	0.5	100.0	0.0047	0.384	0.363	0.00875	3.56
2	25	0.7	50.3	0.0000	0.113	0.000	0.00875	3.48
3	30	0.6	142.7	0.0068	0.393	0.182	0.00875	3.30
4	55	0.6	439.0	0.0626	0.568	0.244	0.00875	2.38
5	25	0.6	102.0	0.0000	0.306	0.065	0.00875	3.71
6	80	0.6	524.1	0.0787	0.773	0.302	0.00875	1.78

[a] The values of resins 1-4 are from Garcia-Diego and Cuellar (2005).

2.2 Sulfonation of beads and resin characterization
The sulfonation procedure for raw poly(ST-co-DVB) beads has been reported previously (Toro, 2008). The quantitative extent of the sulfonation reaction was evaluated by measurement of the ion exchange capacity of each resin, using the standard procedure (Toro, 2008) for polystyrene cation-exchange resins.

3. Results and discussion

3.1 Modeling of the sulfonation process
The sulfonation reaction can be written as:

$$H_2SO_4\ (l) + poly(ST\text{-}co\text{-}DVB)(s) \rightarrow poly(ST\text{-}co\text{-}DVB)\text{-}SO_3^-\ H^+\ (s) + H_2O(l).$$
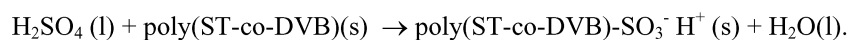
In order to test a mathematical model for the sulfonation of polymeric microparticles, it is initially appropriate to observe the progress of the sulfonation process in Fig. 1.
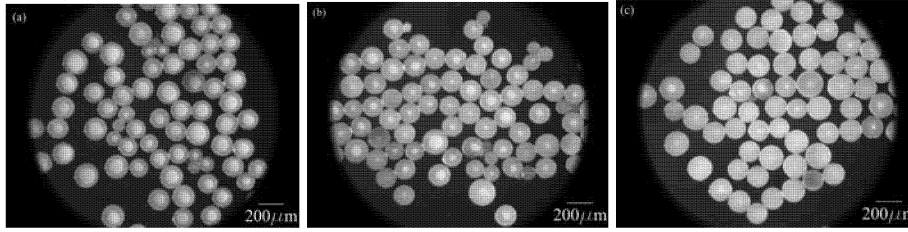

Figure 1. Light microscopy photographs of polymeric microparticles with 25% DVB and 0.5 of Fm, sulfonated with reaction times of (a) 30 min, (b) 120 min and (c)240 min.

In these figures it is possible to observe the existence inside the microparticles of spherical unreacted cores, which progressively shrink as the reaction time progresses. This suggests that, after the external surface of the microparticles has been sulfonated the reaction progresses due to the diffusion of the acid through the porous layer of the product formed around the unreacted core of raw polymer, which should be impervious to the liquid due its hydrophobic character. The reaction must therefore occur at the interface between the product layer and the unreacted core.

Two possibilities can be invoked to account for this scenario. 1) Assuming that the chemical reaction is rate controlling, diffusion could be a relatively fast process and there would therefore be only a small concentration gradient of acid inside the product layer, the reaction taking place in a narrow zone (interface) that moves slowly and progressively from the outer surface to the center of the particle. 2) In contrast, if the diffusion of the acid is the rate controlling factor, the concentration of the acid would fall to zero at the reaction front. In this case, one would be dealing with a concentration gradient of the acid in the product layer and sulfonation would also progress slowly owing to the low acid concentration at the reaction front.

Usually, in the case of non-catalytic fluid-solid reactions with simultaneous diffusion and chemical reaction, a mass balance for the reactant, in a differential volume element of a spherical microparticle, contains an accumulation term, a term related to transport by effective diffusion, and a reaction term. However, this case seems to be a process that can be clearly described by the heterogeneous shrinking-core model. In this model, the mass balance is applied in the layer of product and the reaction term only appears as a boundary condition at the reaction front. Additionally, to simplify the mathematical solution of the model it is customary to neglect the accumulation term in the differential balance (pseudo-steady-state approximation). This assumption should be valid in the first case commented above and is also usually valid in the second case if the density of the fluid in the pores of the product layer is small (gases) with respect to the density of the solid reactant.

To establish a complete model of the process the external mass transfer must also be considered and, in this case, two different possibilities appear: A) infinite-volume condition, if it is considered that the concentration of the liquid reactant does not diminish during the reaction, and B) finite-volume condition, if this concentration diminishes.

Taking into account all the possibilities, many different models can be devised. Some of them were tested with our experimental results.

3.2 Models with pseudo-steady-state

3.2.A) Shrinking-core model with infinite volume and pseudo-steady-state, irreversible, isothermal and first order reaction.

From this model, equation (1) can be derived (Smith, 1970), which gives the dependence of conversion on the reaction time.

$$\frac{M_B k (C_A)_b}{\rho_B r_s} t = \left[1 - (1 - x_B)^{1/3}\right] \left\{ 1 + \frac{Y_1 Y_2}{3}\left[(1 - x_B)^{2/3} + (1 - x_B)^{1/3} + 1\right] + \frac{Y_2}{6}\left[(1 - x_B)^{1/3} + 1 - 2(1 - x_B)^{2/3}\right] \right\}$$

(1)

where: $Y_1 = \dfrac{D_e}{k_m r_s}$; $Y_2 = \dfrac{k r_s}{D_e}$

However, when not all three resistances (external diffusion, internal diffusion and reaction resistances) are significant, equation (1) can be simplified and solutions have been derived (Smith, 1970) for the cases of chemical reaction controlling, diffusion through product controlling and chemical reaction and diffusion through product controlling.

3.2.B) Shrinking-core model with finite volume and pseudo-steady-state, irreversible, isothermal and first order reaction.

When external mass-transfer resistance cannot be neglected, the following solution has been given (Weaver and Carta, 1996).

$$\frac{D_e C_0}{r_p^2 q_m} t = \left(1 - \frac{1}{B_i}\right) I_2 - I_1$$

(2)

The meanings of each of the symbols in equation (2) are also given by Weaver and Carta (1996).

3.3 Models with non-steady-state

As stated before, if the diffusion of the acid is rate controlling, the concentration of the acid drops to zero in the reaction front. In this case, considering non-steady-state, a mass balance for the acid in the product layer takes the form

$$\frac{\partial C_A}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left[r^2\left(\frac{\partial C_A}{\partial r}\right)\right]$$

(3)

The effect of the chemical reaction is to slow down the diffusion process and hence the diffusion coefficient D_s includes the effect of the reaction.

Equation (3) has been solved in the cases of finite and infinite volume.

3.3.A) Shrinking core model with non-steady-state and finite volume

The solution of equation (3) reported by Cranck (1975) is.

$$\frac{q}{q_m} = 1 - 6 \sum_{n=1}^{\infty} \frac{\exp\left(-D_s P_n^2 t / r_p^2\right)}{9\Lambda / (1 - \Lambda) + (1 - \Lambda) P_n^2}$$

(4)

where: $\Lambda = \dfrac{V_M q_m}{V C_0}$; and P_n are the non-zero roots of: $\tan P_n = \dfrac{3P_n}{3 + (1/\Lambda - 1)P_n^2}$ $\qquad$ (5)

3.3.B) Shrinking core model with non-steady-state and infinite volume
The solution of equation (3) reported by Cranck (1975) is, in this case:

$$\frac{q}{q_m} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_s n^2 \pi^2 t}{r_p^2} \right) \qquad (6)$$

3.3.C) Shrinking core model with non-steady-state, infinite solution volume and an interdiffusion coefficient.
In the study of the kinetics of ion-exchange in spherical resins, an interdiffusion coefficient has been used by Helfferich and Plesset (1958). In the case of sulfonation, it can be assumed that the water formed in the chemical reaction exerts some sort of effect on the diffusion coefficient and that this is concentration-dependent. Equation (3), with an interdiffusion coefficient, has been solved numerically but its numerical solution can be expressed by the explicit approximation given by Helfferich and Plesset (1958).

$$\frac{\overline{q}}{q_m} = \left\{ 1 - \exp\left[\pi^2 (-\tau_D + 0,96\tau_D^2 - 2,92\tau_D^3) \right] \right\}^{1/2} \qquad (7)$$

where $\qquad \tau_D = \dfrac{D_s t}{r_p^2}$

3.4 Fitting of the models
The models represented by the equations (1-7) and the above-mentioned simplifications of equation (1) were tested with our experimental data. The best results, shown in Fig. 2 2, were obtained with the model that takes into account a non-steady-state and an infinite volume, along with a complex diffusion coefficient (equation 7).
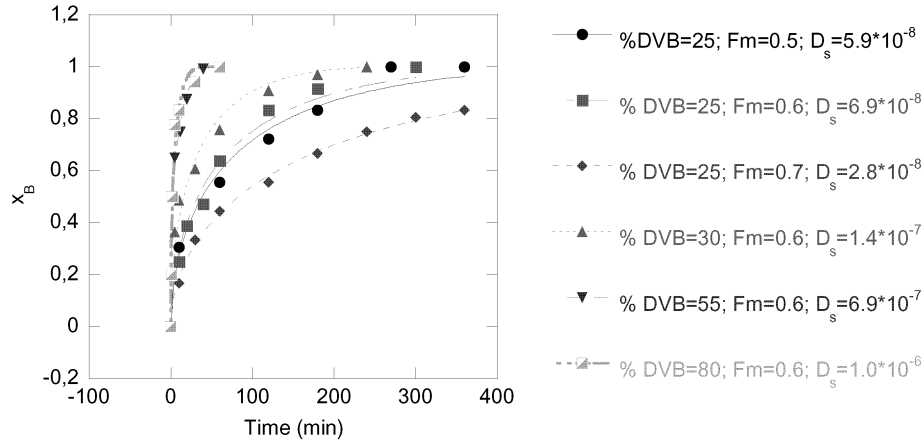

Figure 2. Kinetic curves of sulfonation. Points correspond to the experimental results and lines to the fitted model.

4. Conclusions

The results indicate that the global kinetic of the sulfonation reaction is controlled by the diffusion of the sulfonation agent through the porous product layer, due to the concentration gradient of acid. The model which best fit the experimental data considers non-steady-state and uses a diffusion coefficient concentration-dependent. Regarding the values of the diffusion coefficients, it has been found that the higher %DVB, the higher their values. This can be explained taking into account that the pore volume (micro-, meso- and macro) increases when the %DVB is higher (Table 1) and this facilitates the diffusion of the acid. The influence of the Fm parameter can be extracted from the results of the experiments with 25% DVB: the higher the value of Fm, the lower the volume of the macropores and hence the more the diffusion is hindered.

Nomenclature

C_A: concentration of sulphuric acid in pore, (mol/cm^3)

$(C_A)_b$: concentration of sulphuric acid in bulk phase, (mol/cm^3)

D_e: effective pore diffusivity, according to Eq 1 and 2 (cm^2/min)

D_s: diffusivity of the sulphuric acid inside the particle according to Eq 3, 4, 6 and 7 (cm^2/min)

k: kinetic coefficient of the chemical reaction according to Eq 1 (cm/min)

k_m: external diffusion coefficient according to Eq 1 (cm/min)

M_B: molecular mass of polymer (g/mol)

q: cation exchange capacity (meq/g)

q_m: maximun cation exchange capacity (meq/g)

r: particle radial coordinate according to Eq 3 (cm)

r_s: particle radius according to Eq 1 (cm)

r_p: particle radius according to Eq 4, 6 and 7 (cm)

t: time (min)

x_B: conversion

ρ_B: polymer density (g/cm^3)

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