Alcohol ethoxylation kinetics: Proton transfer influence on product distribution in microchannels

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ABSTRACT

The influence of the reactor type on the product distribution of the base catalyzed ethoxylation of fatty alcohols was studied.

Commonly, proton exchange equilibrium is assumed when modeling this reaction to calculate the product distribution. The model is applicable for ethoxylates produced in semibatch, but cannot explain the products obtained from a continuous microstructured reactor.

In this work, a non-equilibrium model is proposed to explain the observed distributions. The model is better suited to fit the distribution curves, and was used to determine the kinetic parameters of this reaction.

For the propagation reaction, an activation energy $E_{A,P}$ = 74 kJ mol^{-1} was found, which is in good agreement to literature data. For the proton transfer, activation energies in the range of 56 kJ mol^{-1} to 68 kJ mol^{-1} were observed.

1. Introduction

Fatty alcohol ethoxylation is an important process for the production of nonionic surfactants. In this process, ethylene oxide reacts with long chain alcohols, with either a strong acid or a strong base acting as catalyst. The base catalyzed process has the advantage that virtually no side product is formed, and is therefore almost exclusively applied. In that case, the reaction mechanism is a special type of anionic polymerization, with ethylene oxide being sequentially added to a growing ether chain. This process leads to a statistical distribution of the products, as shown in Fig. 1.

Conventionally the ethoxylation process is carried out in semibatch mode in large stirred tank reactors, where ethylene oxide is slowly added to the reaction mixture in order to control the reaction temperature.

Over the years there have been several attempts to create a continuous process in tubular reactors under intensified process conditions, i.e. at higher temperatures and pressures, to achieve higher space time yields [2–4]. Insufficient heat transfer from the reactor tubes impeded stable reactor operation and prevented industrial utilization.

Recently, several patents and patent applications suggested the use of microreactor technology for the production of alcohol ethoxylates [5–9]. The high specific heat removal rate of microstructured reactors should allow to feed ethylene oxide and the starting alcohol stoichiometrically to the reactor without the risk of reactor runaway. In a previous work [10] we studied the feasibility of this concept, which to our knowledge is the first scientific paper on the use of microreactors for ethoxylation reactions.

While there are several publications that study products from a semibatch reactor at conventional reaction conditions, no publication could be found in literature where the effect of intensified process conditions on the product distribution was discussed.

2. Theory

In this work, the base-catalyzed ethoxylation of octanol was studied. In that reaction, ethylene oxide is added to octanol, with potassium octanolate acting as catalyst. In the following, the non-polar alcohol chain C_8H_{17} is abbreviated with R and ethylene oxide and the C_2H_4O group with EO.

The alcoholate is formed prior to the reaction by dissolving potassium hydroxide in the alcohol and removing water by applying vacuum at elevated temperatures:

$$R\text{—}OH + KOH \rightarrow R\text{—}O^-K^+ + H_2O \uparrow . \tag{1}$$
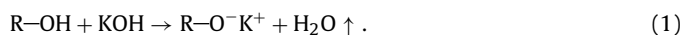
The actual ethoxylation reaction is a S_N2-type polyaddition of ethylene oxide to the alcoholate [11]:

$$R\text{—}[EO]_i\text{—}O^-K^+ + EO \xrightarrow{k_{P,i}} R\text{—}[EO]_{i+1}\text{—}O^-K^+ . \tag{2}$$
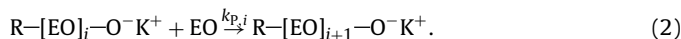
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Fig. 1. Typical distributions of ethoxylate products of various ethoxylation degrees, made in semibatch reactors (from literature [1]).

As there are no chain-terminating reactions, ethoxylation can be considered a special case of living anionic polymerization ("LAP"). The difference to normal LAP lies in the pool of alcohol species present, which is virtually inert to ethylene oxide until activated by the proton transfer

$$R-[EO]_i-O^-K^+ + R-[EO]_j-OH \underset{k_{PT,j,i}}{\overset{k_{PT,i,j}}{\rightleftharpoons}} R-[EO]_i-OH + R-[EO]_j-O^-K^+,$$
(3)

so that while the number of growing chains remains constant, most alcohols will be ethoxylated to a certain degree, resulting in a distribution of the ethoxylate homologues in the product.

Many researchers tried to explain and predict the distribution resulting from these reactions. Early efforts [12–17] were mostly theoretical. There, a simple consecutive mechanism was proposed. In these works, the proton transfer (3) was either neglected, or it was assumed that all of the starting alcohol is converted to alkoxide form, which gives the same result. In [12], a distribution formula
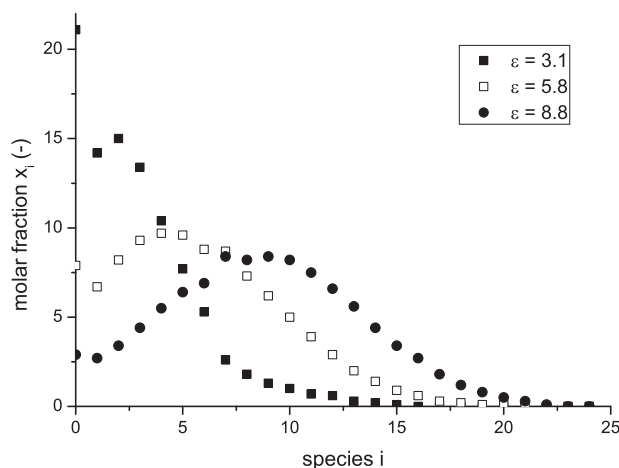
is derived for the case that all propagation rate constants $k_{P,i}$ in reaction (2) are equal. This was later refined to incorporate a differing first rate constant $k_{P,0} \neq k_P$ [14], or that all rate constants $k_{P,i}$ can vary independently [13,15–17].

While it was already recognized rather early that the proton transfer reaction (3) plays a role in that reaction [18], it took some time until improved models were developed which provided for that fact. These models postulate that the proton transfer is very fast, so that equilibrium between the different alcohol and alkoxide species is reached [19–21]. This is understandable, as proton exchange reactions are commonly considered virtually instantaneous. But one has to keep in mind that most reactions in which proton transfer equilibria play a role are conducted in aqueous media, which greatly increases the proton transfer rates by the so-called Grotthuss mechanism [22]. In the case of alcohol ethoxylation, the proton mobility is significantly reduced as no water is present.

In the model proposed by Santacesaria et al. [20] it is assumed that the propagation rate k_P is the same for all ethoxylate species i. Fitting is done by adjusting k_P and the equilibrium constant $K_{PT,i,0} = k_{PT,i,0}/k_{PT,0,i}$, which is assumed to be identical for all i. This simple model with only two variable parameters is able to fit a given distribution reasonably well. However, especially the amount of unreacted alcohol is frequently heavily overestimated.

In [19], so-called oligomer reactivity coefficients ("ORC"s) are used to fit the product distributions, which differ for the various ethoxylate species i. Very close agreements between measured and simulated distributions are possible. The downside is that many fitting parameters are used, and no consistent set of parameters was found to explain all experiments.

In this work, a simple model with only 2 variable parameters is proposed, which overcomes many of the aforementioned drawbacks. The main difference to the literature models is that no proton transfer equilibrium is assumed. Rather, all proton transfer reactions (3) are modeled individually.

The propagation reaction (2) proceeds as first order in alkoxide and ethylene oxide

$$r_{P,i} = k_{P,i} \cdot c_{REO_iO^-K^+} \cdot c_{EO}$$
(4)

and the proton transfer is a bimolecular reaction as well:

$$r_{PT,i,j} = k_{PT,i,j} \cdot c_{REO_iO^-K^+} \cdot c_{REO_jOH}.$$
(5)