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Kinetics of a catalyzed semi-batch ethoxylation of nonylphenol

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ABSTRACT

A combined experiments and mathematical modelling were carried out to study the kinetics of nonylphenol ethoxylation. Experiments were carried out in a well-stirred reactor used in an industrial research laboratory. The governing equations of the kinetic model were solved using Mathematica (2009). Results were validated against published kinetic data. The experiments and kinetics modelling were extended to account the presence of nitrogen in the vapour phase for a potassium hydroxide catalyzed ethoxylation of nonylphenol in a well-stirred reactor. The modelling results were successfully validated against the experimental data. This model has been successfully used (Chiu et al., 2008) for optimizing the productivity of the existing alkoxylation reactors and can be used as a tool for the exploration and design of innovative new reactor systems.

1. Introduction

Non-ionic surfactants, which are poly-alkoxylated derivatives of compounds containing an active hydrogen atom, are important ingredients in domestic and industrial detergents. Alkoxylated non-ionic surfactants are formed in a reaction between an alkoxide (ethylene oxide and/or propylene oxide) with hydrophobes such as fatty alcohols, alkyl-phenols, fatty amines or fatty acids, in the presence of an alkaline homogenous catalyst, normally either sodium or potassium hydroxide (Schick, 1967). In industrial production, this highly exothermic reaction is normally conducted between 140–180 °C and 2–5 atm. Alkoxylation is typical of gas–liquid reactions in which the gaseous reactant (alkoxide) must be transferred and absorbed into the liquid phase prior to reaction. Hence, the overall rate of polyethoxylation is influenced by both mass transfer and reaction kinetics.

In the operation of existing industrial alkoxylation reactors, the semi-batch stirred tank is used. This approach involves promoting the dispersion of gaseous ethylene oxide into liquid hydrophobe. Understanding of the rate phenomena inside the reactors is still rudimentary. There is as yet no working model that can be used with confidence to describe the various simultaneous rate phenomena in operation. Optimization of the productivity of the existing alkoxylation reactor and improvement of the reactor design are extremely difficult and by necessity, empirical. Hence, a collaborative industry–university research project has been initiated to develop a practical and robust model of a semi-batch stirred tank reactor manufacturing non-ionic surfactants. This model has been successfully used (Chiu et al., 2008) for optimizing the productivity of the existing alkoxylation reactors and can be used as a tool providing for the exploration and design of innovative new reactor systems. The ethoxylation kinetics from the present study was integrated into the numerical model (Chiu et al., 2008) for simulating the ethoxylation process. The computed results of both the ethylene oxide consumption and the temperature calculation compared very well with the measurements in the laboratory-autoclave operations. Reasonably good agreement was also reached between the simulated and experimental data on the time-dependent changes of ethylene oxide mass fraction in the bulk liquid in the industrial ethoxylation operations.

Despite the importance of the industrial use of the synthetic non-ionic surfactants, there is limited published information on the kinetic aspects of alkoxylation (Hall and Agrawal, 1990; Santacesaria et al., 1990; Santacesaria et al., 1991; Santacesaria et al., 1992a, b; Di Serio et al., 1994; Di Serio et al., 1995; Di Serio et al., 1996). Within the limited information, there are only two studies, presented in Santacesaria et al. (1990) and Santacesaria et al. (1991), which were devoted to the kinetics of alkylphenol polyethoxylation in the presence of basic catalyst. This established a simple kinetic model which satisfactorily interpreted the kinetic data collected from an isothermal semi-batch ethoxylation reactor. The model described the evolution with time of both

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ethylene oxide consumption and molecular weight distribution for different temperatures, ethylene oxide pressure and catalyst concentration. To safeguard against the explosion hazard in high temperature operation, a blanket of nitrogen pressure is inserted into the reactor at the start of an ethoxylation run. In this paper, we aim to validate the published kinetics (Di Serio et al., 1995) and extend the previous-mentioned model (Santacesaria et al., 1990; Santacesaria et al., 1991) by taking into account the presence of nitrogen in the vapour phase for a potassium hydroxide catalyzed ethoxylation of nonylphenol in a well-stirred reactor used in an industrial research laboratory. This presence of nitrogen reduces the partial pressure of ethylene oxide and hence reduces its reaction rate.

2. The reaction scheme

The overall reaction of ethylene oxide addition to phenol takes place in two steps: the formation of the monoadduct of ethylene oxide to the fresh phenol, followed by a series of ethylene oxide additions to form subsequent adducts. Because phenol has an acidic character, the effect for the ionic couple observed by Santacesaria et al. (1992a, b) for the mechanism of fatty alcohol ethoxylation is less important (Santacesaria et al., 1990). The reaction steps which involve potassium hydroxide as the catalyst are therefore expressed as follows (Schick, 1967; Santacesaria et al., 1990):

[I] The activation step: Refers to activation of the initiator by the basic catalyst, resulting in the metallic salt of the deprotonated initiator RX– and water.

$$\mathrm{RXH+KOHYRX^-K^+ +H_2OZ} \tag{1}$$

[II] The initiation step: The initiation step involves the ethylene oxide addition to the deprotonated initiator RX–. The step is categorised as a nucleophilic substitution.

$$\mathrm{RX^- + EO} \xrightarrow{k_{init}} \mathrm{RX(EO)_1^-} \tag{2}$$

where the rate constant is k_{init}.

[III] The chain transfer equilibrium reaction: The chain transfer equilibrium reaction is accompanied by the initiation reaction. This is the fastest step in the overall reaction because of the involvement of acid–base proton transfer. This effect is thermodynamic rather than kinetic (Hall and Agrawal, 1990). In the case of phenol the acidity of phenol is greater than that of the subsequent polyoxyethylene adducts, the thermodynamic equilibrium is heavily favoured towards the right of Eq. (3)

$$\mathrm{RXH + RX(EO)_i^-} \leftrightarrow \mathrm{RX^- + RX(EO)_iH} \tag{3}$$

[IV] The propagation step: The propagation step is the subsequent polymerisation reaction steps to insert more EO adducts to the substrate at an identical kinetic rate, k_{prop}, due to the similarity in the structure and acidity of the polyethoxylated species $\mathrm{RXE_iO^-K^+}$ (Shachat and Greenwald, 1967)

$$\mathrm{RX(EO)_1^- + EO} \xrightarrow{k_{prop}} \mathrm{RX(EO)_2^-} \ldots\mathrm{RX(EO)_i^- + EO} \xrightarrow{k_{prop}} \mathrm{RX(EO)_{i+1}^-} \tag{4}$$

where i=l,…,n is the number of ethylene oxide unit.

[V] Accompanying proton transfer equilibria:

$$\mathrm{RX(EO)_iH + RX(EO)_j^-} \leftrightarrow \mathrm{RX(EO)_i + RX(EO)_jH} \tag{5}$$

where $i \neq j$.

Accompanying proton transfer equilibria occur simultaneously with the ethoxylation reactions. These polyoxyethylene products are also compounds containing an active hydrogen atom and their corresponding anions are more nucleophilic than the phenoxide ion when phenol is the initiator. Therefore, the propagation steps occur at a higher reaction rate than the initiation step (Lowe and Weibull, 1954).

[VI] Termination reaction: There is no termination reaction. Polymerisation continues until all the ethylene oxide has reacted or until the base is neutralised (Shachat and Greenwald, 1967).

3. The mathematical model

3.1. Governing equations

The mathematical description of the above-mentioned ethoxylation scheme can be expressed in terms of concentration by the differential equations

$$\frac{dm_0}{dt} = -k_{init} \times [\mathrm{RX^-}][\mathrm{EO}]_b$$
$$\frac{dm_1}{dt} = [\mathrm{EO}]_b \times (k_{init}[\mathrm{RX^-}] - k_{prop}[\mathrm{RX(EO)_1^-}])\ldots.$$
$$\frac{dm_i}{dt} = k_{prop} \times [\mathrm{EO}]_b \times ([\mathrm{RX(EO)_{i-1}^-}] - [\mathrm{RX(EO)_i^-}]) \tag{6}$$

where k_{init} is the second order rate constant for the initiation reaction (Eq. (2)), K_{prop} is the second order rate constant for the initiation reaction (Eq. (4)), m_0=[RXH]+[RX], that is the total concentration of alkylphenol and m_i=[RX(EO)$_i$H]+[RX(EO)$_i{}^-$] with i=1 to n

The symbol [ ] represents the concentration of a species and $[\mathrm{EO}]_b$ is the ethylene oxide concentration in the bulk liquid.

In each ethoxylation step, there is one ethylene oxide molecule that is consumed. Thus the overall consumption of ethylene oxide can be written as:

$$\frac{d[\mathrm{EO}]_b}{dt} = [\mathrm{EO}]_b \times \left(k_{init}[\mathrm{RX^-}] - k_{prop}\sum_{i=1}[\mathrm{RX}(EO)_1^-]\right) \tag{7}$$

The number of the differential equations to be solved is dependent on the number of ethylene oxide adducts in the final product. Ethoxylation of nonylphenol in the presence of a basic catalyst is classified as a moderately slow gas–liquid reaction and probably occurs dominantly in the bulk liquid. The process is considered essentially one of physical absorption followed by reaction in the bulk liquid (Santacesaria et al., 1990). The overall reaction is hence influenced by the mass-transfer and kinetic resistance in series. Since the main reaction occurs in the bulk liquid, the liquid side mass-transfer resistance is controlling. The transport of mass between phases is driven by the concentration difference, $[\mathrm{EO}]_{if}-[\mathrm{EO}]_b$, where $[\mathrm{EO}]_{if}$ represents the interfacial concentration of ethylene oxide. The mass transfer rate J characterized by the volumetric mass transfer coefficient k_La is written as

$$J = k_{\mathrm{L}}a \times ([\mathrm{EO}]_{if} - [\mathrm{EO}]_b). \tag{8}$$

Eyhoxylation is typical of moderately slow gas–liquid reactions, with enhancement factor (the ratio of reaction to diffusion) near unity. Which clearly means that eyhoxylation reaction rates are limited by mass transfer hence a steady-state conditions for the ethylene oxide retention can be assumed (Di Serio et al., 1995). By neglecting the initial transient period of reaction for reasons of simplicity, the mass transfer rate of ethylene oxide across phases must be equivalent to the rate of its consumption from the reaction. That is,

$$J = k_La([\mathrm{EO}]_{if}$$
$$- [\mathrm{EO}]_b) = [\mathrm{EO}]_b \times \left(k_{init}[\mathrm{RX^-}] + k_p\sum_{i=1}[\mathrm{RX(EO)}_i]\right) = \frac{d[\mathrm{EO}]_b}{dt} \tag{9}$$