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Large-scale fatty amine ethoxylation reactor: A dynamic model

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Abstract

This case study investigates the behaviour of a plug flow surfactant reactor. The reaction involves adding ethylene oxide to fatty amine to form ethoxylated amines with the assistance of water acting as a catalyst. The reactor was modelled using mass and energy balances plus a description of the kinetics of fatty amine ethoxylation.

Keywords: Fatty amine; Ethylene oxide; Plug flow; Simulation; Reaction kinetics

1. Introduction

Non-ionic surfactants based on ethylene oxide and fatty amines are widely used as detergents, cleaning agents, they are also applied in textiles, oil recovery, etc. [1].

Non-ionic surfactants in question are commercially produced by the reaction of ethylene oxide and fatty amine.

Many authors addressed the kinetics of amine ethoxylation and proposed various models for the reaction [2–9].

Still, application of the kinetic model for the prediction of performance of a real-world reactor is a much more ambitious task.

Nonetheless, there is no such paper taking further step by applying the kinetic model to predict the performance of an industrial reactor. The aim of this work is to fill up this gap and find a way to improve the reactor's operating efficiency.

Quaternary ammonium alkoxides (QAA) that also catalyse ethoxylation are formed in the process as side products. Generally when building a complete process model one should account for their formation. However, when considering the first step (addition of ethylene oxide to amines at temperatures exceeding 120 °C) their formation could be ignored as our experiments showed that concentration of QAA under these conditions in negligible. Autocatalysis of fatty amines ethoxylation in a plug-flow reactor allows to simplify the process and obtain better quality product due to lower polyethylene glycol content. Kinetic studies in the model system butyl amine–ethylene oxide showed the identity of rate laws for hydroxide ethoxylation of alcohols and aminoalcohols.

$$\mathrm{RNH_2} \xrightarrow[\mathrm{C_2H_4O}]{k_0} \mathrm{RNHC_2H_4OH} \xrightarrow[\mathrm{C_2H_4O}]{k_1} \mathrm{RN(C_2H_4OH)_2} \xrightarrow[\mathrm{C_2H_4O}]{k_2} \mathrm{RN(C_2H_4OH)}_n\mathrm{H}$$

where R is alkyl C12–C16, $n = 3$–18.

Only products with 3–12 mol of ethylene oxide per mole of fatty amine have the practical applications.

The industrial ethoxylations are carried out mainly in a batchwise manner at low concentrations of ethylene oxide in the reaction mixture. The significant exotherm makes heat removal a crucial issue, especially due to limitations caused by the product quality deterioration at higher temperatures (products tend to be coloured). There are different ways of carrying out this reaction in the batch reactor. Usually the process is carried out in a semi-batch system with ethylene oxide being fed into the reactor equipped with the mixer and a cooling coil. As the reaction proceeds the reaction mixture gets more viscous lowering the efficiency of mass transfer and, subsequently, the reaction rate. The reaction time is 12–15 h.

The patent proposing to introduce liquid amine into gaseous ethylene oxide greatly increasing the phases' contact surface and shortening the reaction time to 2–3 h was published recently [10].

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Nomenclature

d	pipe diameter (m)
T_{ca}	cooling agent temperature (K)
T_{rm}	temperature of the reaction mixture in the reactor
U	heat transfer coefficient (W/(m^2 K))
w	linear flow rate (m/s)
Greek letters	
μ_{am}	starting fatty amine viscosity (Pa s)
μ_{eo}	ethylene oxide viscosity (Pa s)
μ_{feed}	feed viscosity (Pa s)
μ_{rp}	reaction products viscosity (Pa s)

The productivity could be further increased by switching to a continuous process. There are publications showing the possibility of carrying out the process in a plug flow reactor in a single fluid phase [11].

The large reaction heat (83.8 kJ/mol of added ethylene oxide) puts strict limitations on process parameters (pipe diameter, cooling agent temperature, reactants' ratio, catalyst concentration, etc.). This process is more complicated than ethoxylation of alcohols due to the presence of autocatalysis. This autocatalysis combined with the large reaction heat makes the danger of a thermal runaway quite real. The building of the computer model of the plug flow reactor for amine ethoxylation will be of enormous help in the designing of a large scale process. The development of such a model would allow us to predict the performance of the reactor at different operating conditions. The optimum reaction conditions could be achieved through computer simulation.

2. Kinetics model

A simplified reaction scheme for the polyethoxylation of fatty amines can be expressed in terms of the following two steps:

(1) $\text{R-NH}_2 + \text{C}_2\text{H}_4\text{O} \xrightarrow{\text{Cat}} \text{R-NH-CH}_2\text{CH}_2\text{OH};$
(2) $\text{R-NH-CH}_2\text{CH}_2\text{OH} + \text{C}_2\text{H}_4\text{O} \rightarrow \text{R-N(CH}_2\text{CH}_2\text{OH)}_2.$

where R is alkyl C12–C16, Cat is H_2O.

The non-catalysed reaction is possible but in the presence of water the process is significantly accelerated. All reaction products with significantly acidic properties could also accelerate the reaction [12]. We studied the kinetics of ethoxylation of commercial fatty amines C12–C16 with water content 0.01 mol/L. When the water content is less than 1 mol/L it could be assumed that the catalytic activity of water equals that of the reaction products. That allows us to write the following rate equations:

$$r_1 = r_{\text{n}} + r_{\text{cat1}}$$

$$r_{\text{n}} = k \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}}$$

$$r_{\text{cat1}} = k_1 \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot (C_{\text{H}_2\text{O}} + C_{\text{R-NH-C}_2\text{H}_4\text{OH}} + 2 \cdot C_{\text{R-N(C}_2\text{H}_4\text{OH)2}})$$

$$r_{\text{cat2}} = k_2 \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-C}_2\text{H}_4\text{OH}} \cdot (C_{\text{H}_2\text{O}} + C_{\text{R-NH-C}_2\text{H}_4\text{OH}} + 2 \cdot C_{\text{R-N(C}_2\text{H}_4\text{OH)2}})$$

$$r_2 = r_{\text{n}} + r_{\text{cat2}}$$

where r_{n} is the rate of non-catalytic reaction, r_{cat1} and r_{cat2} the rates of catalysed first and second steps, respectively.

$$k_{\text{n}} = \exp\left(\frac{15.33 - 15128}{T}\right) \quad \text{L/(mol min)}$$

$$k_1 = \exp\left(\frac{11.46 - 5830}{T}\right) \quad \text{L}^2\text{/(mol min)}^2$$

$$k_2 = 0.89 \cdot k_1 \quad \text{L}^2\text{/(mol min)}^2$$

The rate constants for both non-catalytic and catalytic reactions were obtained experimentally (see Section 3).

The reaction rate is described by the following rate equations:

$$\frac{\text{d[R-NH}_2]}{\text{d}t} = k_1 \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot (C_{\text{H}_2\text{O}} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) + k_{\text{n}} \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot \tag{1}$$

$$\begin{aligned}\frac{-\text{d[C}_2\text{H}_4\text{O]}}{\text{d}t} = {} & k_1 \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot (C_{\text{H}_2\text{O}} \\ & + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) \\ & + k_{\text{n}} \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \\ & + k_{\text{n}} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \\ & + k_2 \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{\text{H}_2\text{O}} \\ & + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2})\end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\text{d}[C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}}]}{\text{d}t} \\ = {} & k_1 \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot (C_{\text{H}_2\text{O}} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \\ & + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) + k_{\text{n}} \cdot C_{\text{R-NH}_2} \cdot C_{\text{C}_2\text{H}_4\text{O}} \\ & - k_{\text{n}} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \\ & - k_2 \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{\text{H}_2\text{O}} \\ & + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2})\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\text{d[R-N(CH}_2\text{CH}_2\text{OH]}}{\text{d}t} \\ = {} & k_{\text{n}} \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \\ & + k_2 \cdot C_{\text{C}_2\text{H}_4\text{O}} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{\text{H}_2\text{O}} \\ & + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2})\end{aligned} \tag{4}$$

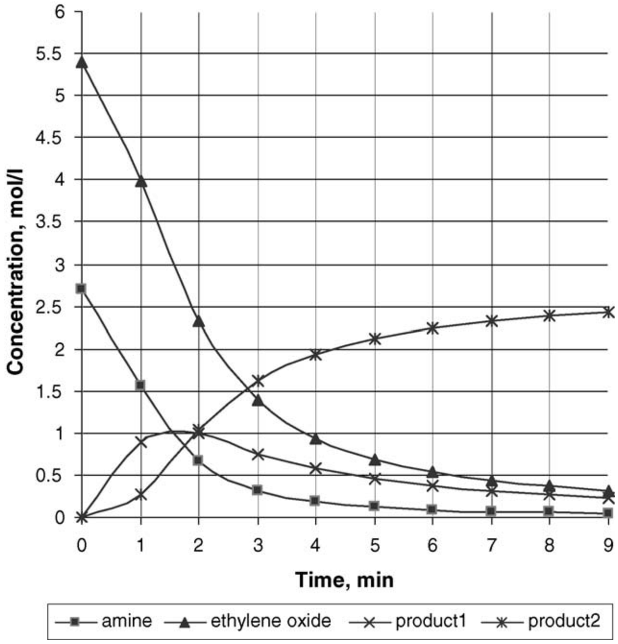

Fig. 1. Concentration profiles (points, experiment; lines, least squares fit).

This system was solved numerically using Runge–Kutta algorithm under following initial conditions—ethylene oxide:amine ratio 2:1, amine average molecular weight 213 and reactants' starting concentrations $C_{C_2H_4O} = 5.4\,\text{mol/L}$; $C_{\text{R-NH}_2} = 2.7\,\text{mol/L}$. The following experimental temperature dependencies of densities were taken into account in our calculations.

$$\rho C_2H_4O = 900.7 - 1.53 \cdot t$$

$$\rho \text{R-NH}_2 = 924 - 0.66 \cdot t$$

t is the temperature in °C. We obtained the following concentration profiles under isothermal conditions ($t = 150\,^\circ\text{C}$). In order to check the developed model we run some experiments in the stainless steel autoclave. The results are shown in Fig. 1.

2.1. Plug flow reactor model

The reactor has been modelled as a plug flow one. The equations of mass, energy balances and kinetics of ethoxylation were simplified subject to the following assumptions:

- the flow is steady, laminar and axial;
- radial velocities are zero;
- axial mass diffusion and energy conduction are small.

$$\frac{d[\text{R-NH}_2]}{dl} = k_1 \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} \cdot (C_{H_2O} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) + k_n \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} \tag{5}$$

$$\frac{-d[C_2H_4O]}{dl} = k_1 \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} \cdot (C_{H_2O} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) + k_n \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} + k_n \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + k_2 \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{H_2O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) \tag{6}$$

$$\frac{d[C_{\text{R-NH-CH}_2\text{CH}_2\text{OH)}_2}]}{dl} = k_1 \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} \cdot (C_{H_2O} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) + k_n \cdot C_{\text{R-NH}_2} \cdot C_{C_2H_4O} - k_n \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} - k_2 \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{H_2O} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) \tag{7}$$

$$\frac{d[\text{R-N(CH}_2\text{CH}_2\text{OH]}}{dl} = k_n \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + k_2 \cdot C_{C_2H_4O} \cdot C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} \cdot (C_{H_2O} + C_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} + 2 \cdot C_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2}) \tag{8}$$

This system was solved together with the energy balance equation.

2.1.1. Energy balance equation for a plug flow reactor

$$\sum(-\Delta H_i) \cdot r_i + \frac{4}{d} \cdot U \cdot (T_{\text{ca}} - T_{\text{rm}}) = (w \cdot \sum C_{\text{J}} \cdot \text{Cp}_{\text{J}}) \frac{dT}{dl} \tag{9}$$

The heat of the reaction ΔH is $-100.56\,\text{kJ/mol}$.

The molar heat capacities of reactants and products were calculated according to the equation [13,14]:

$$\text{Cp} = \sum n_i a_i + \sum n_i b_i T + \sum n_i c_i T^3 + \sum n_i d_i T^3 \tag{10}$$

The following values of molar and mass heat capacities were obtained:

$$\text{Cp}_{\text{R-NH}_2} = 498.8\,\text{J/mol}; \qquad \text{Cpm}_{\text{R-NH}_2} = 2342\,\text{J/kg}$$

$$\text{Cp}_{C_2H_4O} = 80.41\,\text{J/mol}; \qquad \text{Cpm}_{C_2H_4O} = 1828\,\text{J/kg}$$

$$\text{Cp}_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} = 576.4\,\text{J/mol}; \quad \text{Cpm}_{\text{R-NH-CH}_2\text{CH}_2\text{OH}} = 2243\,\text{J/kg}$$

$$\text{Cp}_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2} = 672.7\,\text{J/mol}; \quad \text{Cpm}_{\text{R-N(CH}_2\text{CH}_2\text{OH)}_2} = 2235\,\text{J/mol}$$

$$\text{Cpm (rm)} = 2159\,\text{J/kg}$$

2.1.2. Viscosity calculations

Kinematical viscosities for the starting amine C_{12}–C_{16} and ethoxylation products were determined experimentally.

$$y = \exp\left(\frac{a}{t + 273} - b\right),$$

centistokes, $a = 1747$; $b = 4.39$. Kinematical viscosity of the starting amine and reaction products at 180 °C is $5.866 \times 10^{-7}\ \mathrm{m^2/s}$.

$$\mu_{\mathrm{am}} = 4.72 \times 10^{-4}\ \mathrm{Pa\,s};$$

$$\mu_{\mathrm{rp}} = 5.40 \times 10^{-4}\ \mathrm{Pa\,s};$$

$$\mu_{\mathrm{eo}} = 0.1 \times 10^{-4}\ \mathrm{Pa\,s};$$

$$\mu_{\mathrm{feed}} = \frac{1}{3}\mu_{\mathrm{am}} + \frac{2}{3}\mu_{\mathrm{eo}} = 2.24 \times 10^{-4}\ \mathrm{Pa\,s};$$

$$\log \mu_{\mathrm{rm}} = \frac{1}{2}(\log \mu_{\mathrm{feed}} + \mu_{\mathrm{rp}}); \quad \mu_{\mathrm{rm}} = 3.37 \times 10^{-4}\ \mathrm{Pa\,s};$$

Thermal conductivity of the reaction mixture was calculated by the equation $\lambda = 0.17 - 0.00019t$ [15], $\lambda_{\mathrm{rm}} = 0.136\ \mathrm{W/(m\,K)}$.

The value of the heat transfer coefficient is necessary for the building of the complete reactor model. It could be estimated by Eq. (1) recommended for circular pipes under turbulent flow regime [16]. For example, for $d = 0.068$ m and $Re = 11{,}000$.

The Prandtl number,

$$Pr = \frac{\mathrm{Cpm} \cdot \mu_{\mathrm{rm}}}{\lambda_{\mathrm{rm}}};$$

the Nusselt number $Nu = 0.023 \cdot 11000^{0.8} \cdot 5.996^{0.3} = 67.2$ (1) and $U = 134\ \mathrm{W/(m^2\,K)}$.

It is seen that calculations using dimensionless groups (the Reynolds, Prandtl and Nusselt numbers) give the underestimated value of the heat transfer coefficient [17]. The higher values of the heat transfer coefficient were also obtained in ethoxylation of fatty alcohols C_{12}–C_{16} on the pilot unit at Shebekino Chemical Plant [18].

The value of the heat transfer coefficient in the energy balance was recalculated using the data [15]. The coil 9 mm diameter and 12.5 m length immersed in water boiling under increased pressure was used in the experiments [15] as the reactor. Reactants preheated to 100 °C were fed into the reactor. Authors measured the temperature profile along the reactor length. The heat transfer coefficient for the simulation was determined comparing temperature profiles along the reactor length obtained by the numerical integration of our model and the real ones. As could be seen from Fig. 2 the best agreement was at $U = 450\ \mathrm{W/(m^2\,K)}$. Fig. 2 shows experimental [15] and predicted temperature profiles.

The following dimensionless Eq. (11) is recommended for the transient flow regime at Reynolds number in the range 2000–7000 [16].

$$Nu = 0.008 \cdot Re0.9 \cdot Pr0.43 \qquad (11)$$

Umbach and Stein [15] used the following experimental conditions—$T_{\mathrm{ca}} = 503$ K, $d = 0.009$ m, $w = 0.19$ m/s, molar ratio fatty amine:ethylene oxide = 1:1, average $T_{\mathrm{rm}} = 453$ K. The value of the heat transfer coefficient calculated by Eq. (11) from data [15] is $422\ \mathrm{W/(m^2\,K)}$. It should be noted that the error margin for the values of the heat transfer coefficient obtained with the help of dimensionless parameters is about ±20%. It reflects on the incompleteness of our knowledge rather than the inaccuracy of the measurements. So the agreement of values obtained according to the mathematical model and by Eq. (11) is quite satisfactory.

It was necessary to adjust the heat transfer coefficient for our initial conditions as assumed reactants ratio amine:ethylene

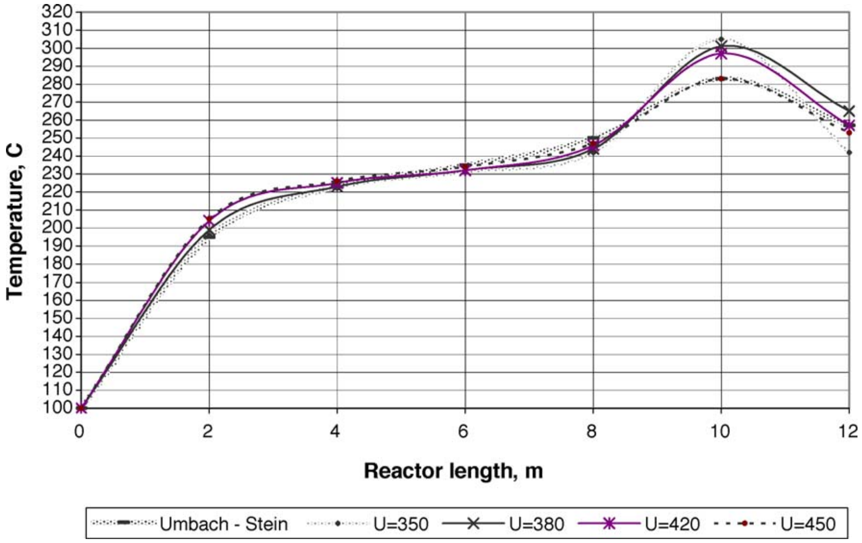

Fig. 2. Determination of the heat transfer coefficient.

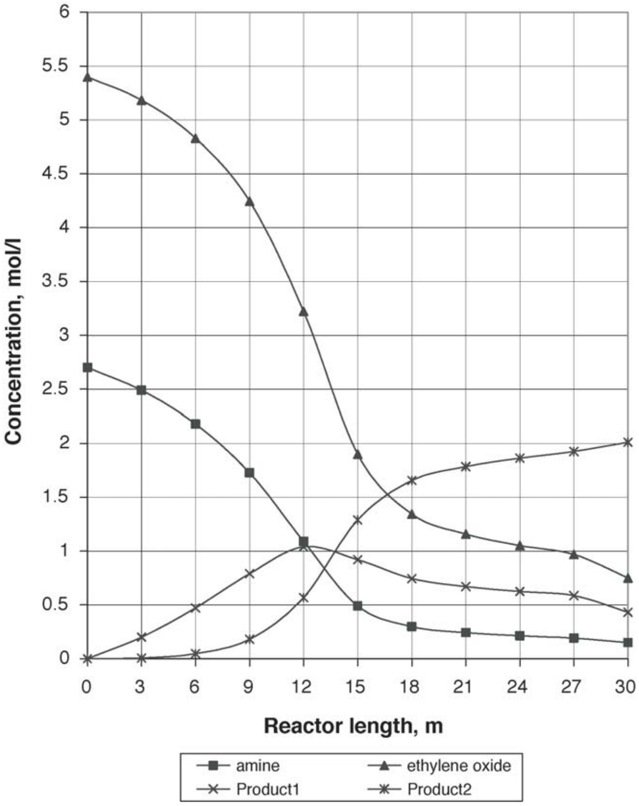

Fig. 3. Concentration profiles along the reactor length.

oxide 1:2 was different from one employed by authors in Ref. [15]. The adjusted value was 650 W/(m^2 K). At pipe diameter 0.068 m, Reynolds number *Re* 7000 and linear flow velocity 2.6 m/min the following concentration and temperature profiles were obtained (Figs. 3 and 4).

Boiling water was used as the cooling agent and maximum reactor temperature was 417 K.

Under these conditions the pressure in the reactor will be 0.92 MPa.

Let us consider the stability of the model.

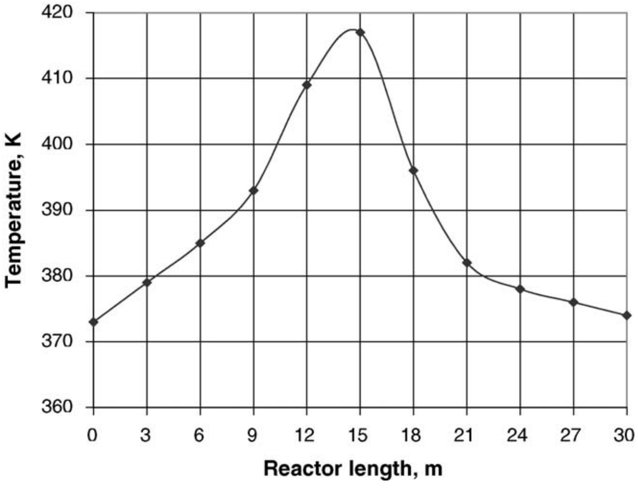

Fig. 4. Temperature profile along the reactor length.

We assumed the turbulent flow with Reynolds number $Re = 11{,}000$ and determined linear velocities providing for this flow at standard pipe diameters.

We determined temperatures at different pipe diameters assuming $U = 250$ W/(m^2 K).

The value of the heat transfer coefficient was chosen for the worst-case real world reactor operation conditions: when tars that greatly increase thermal resistance are deposited on the inside wall.

The values of reactor temperature and ethylene oxide conversion were obtained by the numerical integration of the model. Molar ratio fatty amine:ethylene oxide was 1:2, heat carrier temperature 100 °C (boiling water), initial temperature of the reaction mixture 100 °C. The integration was run up to 99% conversion degree. Results are listed in Table 1.

The maximum reactor temperature is limited by the product quality requirements (at high temperatures the product becomes coloured). It is clearly seen that in the framework of the model the range of reactor diameters when the reaction temperature does not exceed 480 K, i.e. providing for the acceptable product quality is quite limited. Model predicts severe constrains in the choice of diameter and length of reactor tubes. It would be hardly possible to build the reactor with the tube length 300 m as the hydrodynamic resistance will be extremely high. Thus the acceptable range of tube diameter is 0.032–0.04 m and length 50–100 m. The sensitivity of the temperature profile to the variation of parameters depends on their starting set [19]. In our case the model stability is increased with decreasing the pipe diameter and molar ratio ethylene oxide–fatty amine. The stability is also increased with growth of the heat carrier temperature and reactants' feed linear rate. The model is most sensitive to the variations in heat carrier temperature. Under certain conditions the change of heat carrier temperature on 1 °C could result in great variations in the reactor temperature (up to 100 °C). The analysis of the model behaviour with the following constraints: heat carrier temperature variation ±5 °C and reactor temperature variation ±50 °C revealed that at pipe diameter 0.045 m the model sensitivity exceeds the acceptable limit of 10 °C/1 °C.

The results demonstrated that when all ethylene oxide is fed at the reactor inlet the acceptable range of process parameters is very narrow.

Table 1
Reactor temperatures ad different pipe diameters

d (m)	w (m/min)	Reactor length (m)	$T_{\max}$ (K)
0.019	13.9	300	390
0.032	8.25	100	470
0.04	6.6	50	480
0.049	5.4	35	553
0.068	3.9	30	607
0.079	3.33	27	617
0.1	2.65	15	620
0.125	2.10	10	637
0.15	1.8	8	650

Table 2
Composition of fatty amine C_{12}–C_{16} mixture

No.	Amine	Concentration (%)
1	C_{10}	0.06
2	C_{11}	2.87
3	C_{12}	8.69
4	C_{13}	32.55
5	C_{14}	24.20
6	C_{15}	16.54
7	C_{16}	13.79
8	C_{17}	5.70
9	C_{18}	4.30
10	C_{19}	1.30

3. Experimental

3.1. Materials

For kinetic and viscosity measurements the commercial mixture of fatty amines C_{12}–C_{16} produced by Volgodonsk Chemical Plant (Russia) was used. The composition of this mixture determined by GLC analysis is listed in Table 2.

Ethoxylated derivatives of fatty amines were synthesised by heating equimolar quantities of fatty amine and ethylene oxide in stainless steel tubes for 8 h at 110 °C till the complete conversion of ethylene oxide.

3.2. Analyses

GLC analysis was performed on gas chromatograph "Chrom-5" (Laboratorni Pristroje, Czech Republic) with FID. Glass column packed with Chromosorb N-Super with 5% SE-30. Injector temperature 280 °C, oven heating rate 10 °C/min from 80 to 280 °C.

Concentration of starting reactants, reaction products and QAA were determined by potentiometric titration [20].

3.3. Kinetic measurements

Reaction kinetics was studied by manometric method using the following set-up. The reaction mixture (ethylene oxide and fatty amine mixture, total volume 5 mL) was placed into the reactor 1 with a magnetic stirrer and was cooled by liquid nitrogen till the pressure stopped falling. The set-up was evacuated till 1–3 Torr residual pressure and the set-up was placed into a water bath. The reaction progress was monitored by measuring the pressure drop. The vapour phase volume in the set-up was less than 1% of the liquid volume. The Henry constant was independent of ethylene oxide concentration in the range of 0.1–1.0 mol/L Fig. 5.

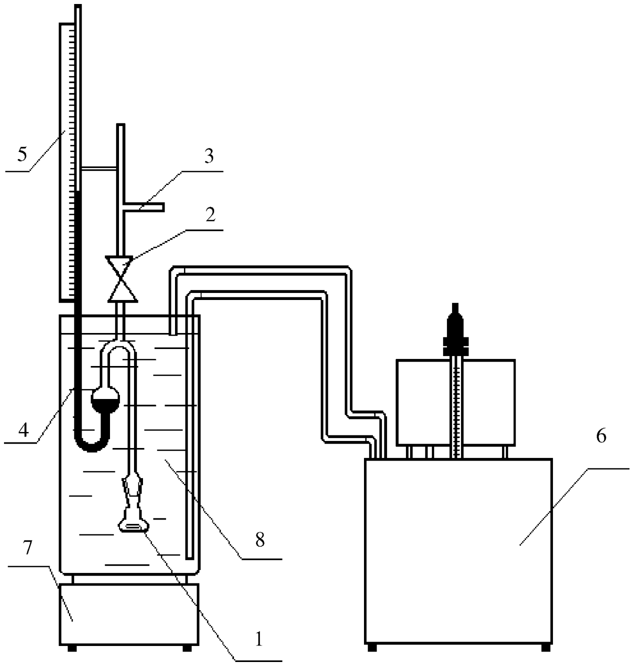

Fig. 5. Experimental setup for kinetic measurements. (1) Reactor; (2) vacuum valve; (3) nipple; (4) mercury cistern manometer; (5) scaleplate; (6) thermostat; (7) magnetic stirrer; (8) bath.

3.4. Viscosity determination

Viscosity of fatty amines and ethoxylated derivatives was determined using efflux viscometer.

4. Conclusion

The work to date has demonstrated how the computer model of the ethoxylation plug flow reactor can be used to predict the performance of a real reactor, i.e. the product distribution and the temperature profile. The results obtained demonstrate high sensitivity of the model to the reaction parameters and severe constrain caused by hydrodynamic restrictions and product quality requirements. The process becomes viable at pipe diameter not exceeding 0.04 m and strictly fixed values of feed linear rate, reactants' ratio and heat carrier temperature.

References

[1] M.J. Schick, Nonionic Surfactants, vol. 1, Marcel Dekker Inc., New York, 1967.
[2] J. Trejbal, M. Petrisko, React. Kinet. Catal. Lett. 82 (2004) 339–346.
[3] M. Mosquet, Y. Chevalier, P. Le Perche, J.P. Guicquero, Macromol. Chem. Phys. 198 (1997) 2457–2474.
[4] J.W. Holubka, R.D. Bach, J.L. Andres, Macromolecules 25 (1992) 1189–1192.
[5] B. Weiland, K. Haage, Abhandlungen der Akademie der Wissenschaften der DDR, Abteilung Mathematik, Naturwissenschaften, Technik (1N) (1987) 595–601.
[6] D. Kamenski, R. Boeva R., N. Stoyanov, Taseva, Igodishnik na Visshiya Khimiko-Tekhnologichen Institut, Burgas 19 (1985) 53–60.
[7] A. Weidenbacher, S. Serban, Revistade Chim. 36 (1985) 21–25.
[8] Y.-S. Ahn, T.-Y. Lee, Y.-K. Chang, C.-B. Chung, S.-K. Ihm, Hwahak Konghak 18 (1980) 393–400.
[9] W. Gestrich, W. Krauss, Ber. Bunsen-Ges. 78 (1974) 1334–1339.
[10] Schubart, Rudiger, Process for the selective preparation of monohydroxyalkylated amines, United States Patent 4,223,138, 1980.
[11] Gibson, A. Charles, Ahmed, Moinuddin, Nelson, R. James, Continuous process for preparing alkanolamines United States Patent 4,847,418, 1989.

[12] N.N. Lebedev, Khimiya i Tekhnologiya Osnovnogo Organicheskogo I Neftekhimicheskogo Sinteza [Chem. Technol. Bulk Organic Petrochem. Synth.] (Russ.).

[13] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, The Properties of Gases and Liquids, third ed., McGraw-Hill, 1987.

[14] R.H. Perry, C.H. Chiltern, D.W. Green, Chemical Engineer's Handbook, 6th ed., McGraw-Hill.

[15] W. Umbach, W. Stein, Fette, Seifen, Anstrichmittel B 71 (1969) 938.

[16] O. Florea, O. Smigelschi, Calcula de Operatii ci Utilage Din Industri Chimica, Editura Technical, Bucuresti, 1966.

[17] Heat Exchanger Design Handbook, vols.1 and 2, Chemisphere Publ. Corp, 1983.

[18] V.F. Shvets, M.G. Makarov, Yu.P. Suchkov, Teoreticheskie Osnovy Khimicheskoi Tekhnologii 17 (1983) 342–346.

[19] D.D. Perlmutter, Stability of Chemical Reactors, Prentice-Hall, NJ, 1972.

[20] S. Siggia, J. Hanna, Quantitative Organic Analysis via Functional Groups, fourth ed., J. Wiley & Sons, NY, 1979.