

Oxyethylation of Fatty Acid Methyl Esters. Molar Ratio and Temperature Effects. Pressure Drop Modeling

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The effect of reagent molar ratio and temperature upon the composition of oxyethylated fatty acid methyl esters and surface tension reduction at air/water interfaces was studied. It was found that oxyethylation of fatty acid methyl esters carried out in the presence of calcium-based catalyst gives narrow range distributed products. The distribution depends on temperature, and more narrow products are obtained at higher temperatures. Oxyethylated fatty acid methyl esters contain less unreacted hydrophobic starter than oxyethylated alcohols. The pressure drop in the batch process can be satisfactorily modeled, assuming the reaction proceeds in the liquid phase and estimating the concentration of the ethylene oxide in the liquid phase from vapor–liquid equilibrium. The modeling supports the important role of ethylene oxide diffusion from the gas to the liquid phase. The distribution of the polyoxyethylene chain in hydrophilic oxyethylated fatty acid methyl esters has only a minor effect upon the surface tension reduction and the values of characteristic adsorption coefficients. The effect of the synthesis temperature is not reflected in the surface tension reduction.

Introduction

Fatty acids obtained from natural renewable resources are an important raw material for nonionic surfactants although a major proportion of surface-active agents consumed today in the industrialized countries is produced from petrochemical sources. However, a trend has developed and is gaining momentum to rely more and more on surfactants from natural-renewable resources.

Natural fats are converted to fatty acids or their methyl esters in typical processes of hydrolysis and methanolysis, respectively. The latter seems now more attractive due to a growing interest in an ecological diesel fuel. Hydrogenolysis of fatty acids and their methyl esters gives alcohols used for the manufacture of nonionic surfactants.

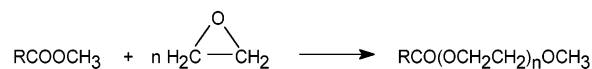
This three-step process could be simplified if surfactants were directly obtained from fatty acids or their methyl esters. The direct synthesis from fats and oils would be the best choice. However, such a process is unrealistic due to the instability of glycerol. The direct oxyethylation of fatty acids^{1–4} gives a complex mixture with enormous amounts of polyoxyethylene glycols and their diesters. Thus, the process is not attractive due to economical aspects and poor quality of the products.

Up to the early 1990s it was assumed that oxyethylation can occur only when the hydrophobic reagent had a labile hydrogen.^{1–3,5} Thus, fatty acid methyl esters were not considered as a raw material for direct synthesis of nonionic surfactants with a polyoxyethylene

chain. However, esters of fatty acids and polyoxyethylene glycol monomethyl ethers were known and their properties described.⁶ They were synthesized in a two-step process. Methanol was oxyethylated to polyoxyethylene glycol monomethyl ether, which was then converted to the final product by transesterification with fatty acid methyl esters or by the esterification with fatty acids carried out in the presence of an alkaline or an acid catalyst, respectively.

Esters of typical nonionics were synthesized in similar ways and their properties described.^{7–9} Fats could be also used in the transesterification step.

The pioneer works of Hoechst,¹⁰ Henkel,¹¹ Vista Chemical Co.,¹² and Lion Corp.¹³ have demonstrated that the direct reaction between fatty acid methyl esters and ethylene oxide can be carried out when new-type catalysts are used. More detailed studies were described by Hama et al.^{14–16}



The first oxyethylene unit is inserted between the carbonyl carbon and methoxy group.¹⁶ The next oxyethylene groups are also inserted between the carbonyl carbon and the oxygen atom of $(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ group. Thus, the process shows important similarities to the polymerization of ethylene carried out in the presence of Ziegler–Natta catalysts. It is surprising that a few decades were needed to transfer the knowledge from polymers to surfactants.

Reaction of fatty acid methyl esters with ethylene oxide needs a weakening or even a breaking of the bond between carbonyl carbon and oxygen of the methoxy group. It is well known that the hydrolysis of esters composed from carboxylic acids and primary alcohols,

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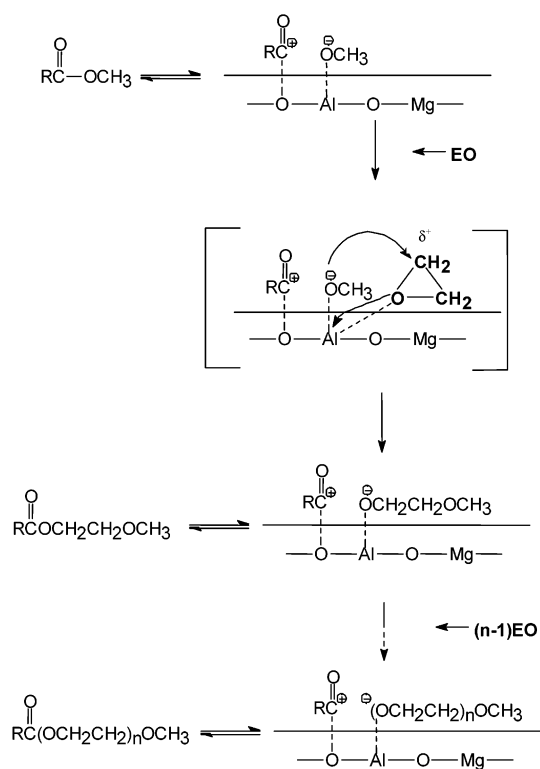


Figure 1. Reaction pathway with dissociative chemisorption.

e.g., fatty acids and methanol, occurs according to the B_{AC}2 or A_{AC}2 mechanisms in the presence of an alkaline or an acidic catalyst, respectively.

The characteristic feature of these reactions is a stability of the intermediate complexes that can even be considered as intermediate products. Furthermore, the stability of the cationic intermediate product is even so high that an exchange of the oxygen atom with a solvent molecule occurs. Each step of the process carried out in the presence of an acidic catalyst is reversible, which means that the original ester or an ester-type product can be regenerated. The intermediate product formed in the presence of an alkaline catalyst is also stable, but each reaction step is irreversible.

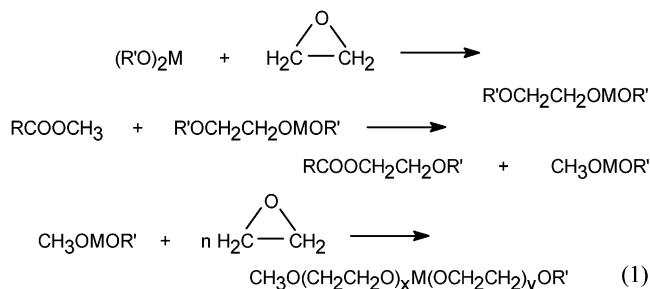
All this means that acidic catalysis has a great potential for a direct reaction of fatty acid methyl esters with ethylene oxide. It is, however, obvious, that typical mineral acids and Lewis acids cannot be used.

The heterogeneous catalysts based on metal oxide composites and hydrotalcite are effective in oxyethylation of fatty acid methyl esters. According to Hama,¹⁷ the dissociative chemisorption of fatty acid methyl esters occurs (Figure 1). The rate of each successive step of oxyethylation is slower due to the competition of the oxygen atoms from the polyoxyethylene chain for the coordination at positive centers with ethylene oxide. As a result, narrow range distributed products are formed.

However, such a mechanism does not explain the reaction carried out in the presence of a calcium-based catalyst modified with acids. An explanation can be an exchange of a water molecule with ethylene oxide in the intermediate product formed on the catalyst surface (A_{AC}2 mechanism). The next step would be the insertion of the oxyethylene group between the carbonyl carbon and the oxygen of the alkoxy group.

The reaction is also possible in the presence of polyvalent hydroxides, e.g., Ba(OH)₂,¹⁰ and especially

in the presence of activated calcium and aluminum alkoxides.¹² The reaction is negligible in the presence of hydroxides and alkoxides of monovalent metals. The following reaction scheme was proposed by Cox and Veerasooriya:¹⁸



where M denotes Ca (but can be also Al).

The catalyst first reacts with ethylene oxide to form the ethoxylated version of the metal alkoxyethoxylate, which partly reacts with methyl ester to form the alkyl ester ethoxylate and metal alkoxide. Further reactions of the metal alkoxide, metal alkoxyethoxylate, or both give metal-coordinated alkoxypolyoxyethylates, which on transesterification with methyl esters produce higher homologues of oxyethylated fatty acid methyl esters. The transesterification reactions are shifted to the right as an excess of methyl ester is present in the reaction mixture with respect to metal alkoxide.

The aim of this work was to study the effect of the reagent molar ratio and temperature on the composition and surface activity of oxyethylated fatty acid methyl esters. Up to now, it was generally accepted that the composition of oxyethylated alcohols did not depend on temperature and such effect was not studied in the oxyethylation of fatty acid methyl esters.

The aim of the work was also to model the oxyethylation of fatty acid methyl esters carried out in an autoclave simulating the drop of pressure.

Experimental Section

Materials. Dodecanol (D; 98% pure, Aldrich), methyl dodecanoate (MD; Edenor 12, 98–100, Henkel), and rape seed fatty acid methyl esters (MRA; Biodiesel Producers Association) were used as hydrophobic reagents. Ethylene oxide was obtained from Mazovian Petrochemical Works (Plock, Poland), and a proprietary calcium-based catalyst came from the Institute of Heavy Organic Synthesis (Kedzierzyn-Kozle, Poland).^{19,20} Calcium acetate monohydrate (15.4 g) and concentrated sulfuric acid (3.8 g) was added to MRA (65 g), and the suspension was mixed vigorously at ambient temperature to fully homogenize the components.

Synthesis. The reaction was performed in a 2-L stainless steel autoclave (Autoclave Engineers, Erie, PA) equipped with a mechanical stirrer and a cooling coil. The reactor was charged with the hydrophobic substrate and the proprietary calcium-based catalyst (DC-L70). The reactor was then closed, and an automated procedure for the synthesis was started. The reactor system was equipped with a programmable logic control system (PLCS) allowing the desired amount of ethylene oxide to be fed under the assumed parameters of pressure and temperature, controlled by the PLCS microprocessor. The mass of the hydrophobic starter was 300 g. The amount of ethylene oxide (EO) was equivalent to the

desired molar ratio of EO to the hydrophobe and was varied from 0.66 to 15. The temperature was controlled and changed from 135 to 185 °C. The maximum pressure was 0.5 MPa, and the reaction was stopped when the pressure decreased to 0.01 MPa.

Gas Chromatographic Analysis. Capillary and packed column gas chromatography²¹ were applied to determine the homologue distribution of directly oxyethylated methyl dodecanoate (MDEO_i) and oxyethylated rape seed fatty acid methyl esters (MRAEO_i) and alcohol oxyethylates (DEO_i) with the average degree of oxyethylation below 15. The determination of fractional composition of the methyl ester oxyethylates was performed using procedures for the analysis of oxyethylated fatty alcohols. However, the derivatization of fatty acid methyl ester could not be carried out, as there was no appropriate functional group to be further converted. For this reason, the products had to be analyzed as they appeared originally. The investigated samples were diluted in benzene prior to the analysis, and the solution was injected into a Perkin-Elmer model 900 chromatograph. The ratio of benzene to oxyethylate sample was 10:1 and 2:1 in the case of capillary and packed column separations, respectively. The following conditions were assumed for the packed column analysis: a stainless steel column (homemade) was used, 0.4 m long and 2.0 mm in diameter, filled with Dexil 400GC on Chromosorb GAW-DMCS. The system allowed for the separation temperature range from 90 to 340 °C. The injector temperature was 380 °C.

The capillary column analyses were performed on a Hewlett-Packard chromatograph, model 5890 series 2, using DB-2HT column (Altech Associates Inc.), 10 m long, 0.32-mm diameter, with the film thickness of 0.1 µm. The separation temperature was programmed from 60 °C up to 340 °C, and the detector temperature was 360 °C.

HPLC Analysis. Liquid adsorption chromatography (LAC) was used to determine the composition of oxyethylated rapeseed acid methyl esters. These measurements were performed using the density detection system DDS70 (Chromtech, Graz, Austria).^{22,23} Data acquisition and processing were performed using the software package CHROMA, which has been developed for the DDS 70. The columns and density cells were placed in a thermostated box, in which a temperature of 25.0 °C was maintained for all measurements.

The mobile phase was delivered by an ISCO 2350 HPLC pump and an ISCO 2360 gradient programmer (from ISCO, Lincoln, NE). The flow rate was 1.0 mL/min in all measurements. Samples were injected using a Spark 125 autosampler equipped with an 20-µL loop. A Waters Spherisorb 5-µm silica column (5 µm, 80 Å, 4.0 × 250 mm, serial no. 025A303061) was used in all LAC measurements. In gradient elution, mobile phase A was ethyl acetate and B was acetone–water 80:20 (w/w). The following gradient profile was used: we started with 100% A and ran in a first section to 75% A within 3 min. The sample was injected after a delay time of 3.5 min. The second section was 22 min from 75% A (25% B) to 100% B, kept at this composition for 5 min, and went back to 100% A in 1 min. A Sedex 45 ELSD (Sedere, France) was connected to the DDS 70. Nitrogen was used as carrier gas, and the pressure at the nebulizer was set to 1.0 bar and the temperature of the evaporator to 30 °C.

Table 1. Properties of Oxyethylated Methyl Dodecanoates for Various Degrees of Oxyethylation As Calculated by Lydersen Methods^a

m_{EO}/m_{MD} (mol/mol)	M	ρ (g/cm ³)	T_C (K)	$P_C \times 10^{-6}$ (Pa)	T_B (K)
0	214.35	1.05	728.1 (712.0) ^b	1.7202 (1.7400) ^b	553.9 (540.0) ^b
1	258.40	1.07	746.0	1.7041	577.1
2	302.45	1.09	792.5	1.5096	626.5
3	346.50	1.11	831.6	1.3544	669.8
4	390.55	1.13	865.7	1.2278	708.3
5	434.60	1.15	895.8	1.1226	742.9
6	478.65	1.16	922.6	1.0339	774.3
7	522.70	1.17	946.9	0.9582	803.0
8	566.75	1.17	968.9	0.8927	829.4
9	610.80	1.17	989.2	0.8355	853.8
10	654.85	1.17	1007.9	0.7853	876.4
11	698.90	1.16	1025.3	0.7407	897.5

^a M , molecular weight; ρ , density; T_C , critical temperature; P_C , critical pressure; T_B , boiling point. ^b Values from measurement.

All solvents were HPLC grade. Acetone was purchased from Roth (Karlsruhe, Germany), and methanol and water were from Riedel-de Haen (Seelze, Germany).

Surface Tension Determination. Measurements of equilibrium surface tension were performed by the ring method at 22 °C, using a K12 tensiometer (Krüss, Germany).

Reagent Properties. There are no experimental data concerning properties of oxyethylated methyl dodecanoate with different numbers of EO groups in the molecule. The properties of compounds (Table 1) were estimated from their molecular weight and molecular structure using Lydersen methods²⁴ for critical parameters and the UNIFAC group contribution method for phase equilibrium.^{24,25}

Densities were determined under the assumption that the influence of the number of oxyethylene groups on density was similar as in the case of other oxyethylated compounds (dodecanoic acid or dodecanol). Actual values for methyl dodecanoate demonstrated acceptable accuracy of calculations. The quality of vapor–liquid equilibrium estimation was verified by comparison of experimental and estimated relationships for the methyl dodecanoate–ethylene oxide system.

Results and Discussion

Modeling of the Batch Process. The reaction of hydrophobic substrates with EO is strongly exothermic. In the equipment used here, equipped with a computer-controlled system, the temperature changes at the steady state only in the range of a few degrees. However, almost 20–30 min is needed to achieve a constant temperature.

Figure 2 shows the change of pressure during the oxyethylation. In this case, the mass of the starter was 300–470 g, and only 41–44 g of EO equivalent to the average degree of oxyethylation equal to 0.66 was introduced at the start of the process. Then, the temperature was increased to reach the desired temperature in the period of 20–25 min. An increase in temperature caused an evaporation of EO and an increase of pressure. A drop of pressure at constant temperature can be a measure of the EO conversion. However, it is seen that a similar induction period connected with the dissolution of catalyst is needed to start the reaction of methyl dodecanoate with EO. The reaction proceeds faster at higher temperature and

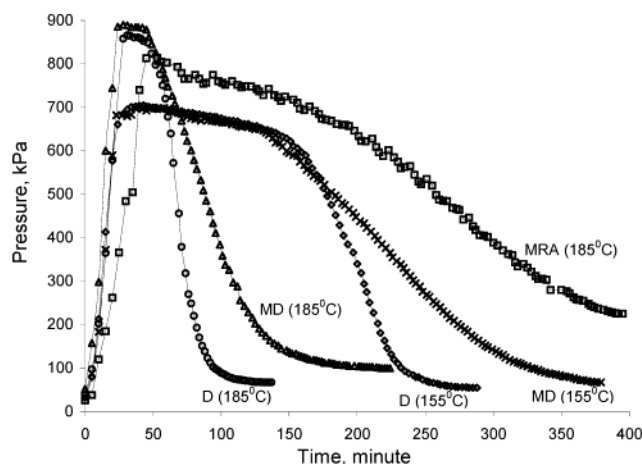
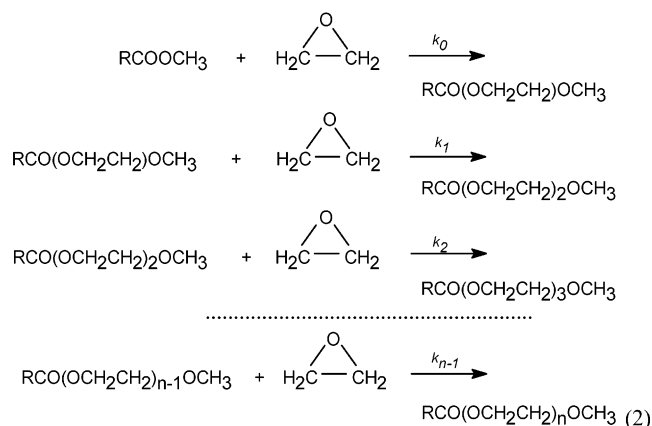


Figure 2. Change of pressure during the oxyethylation reaction ($i = 0.66$).

when alcohol is used as a starting material. The slow down of EO conversion observed in the case of fatty acid methyl esters may be caused by a different mechanism but also by a lower solubility of EO in the less polar starting material.

Oxyethylation is a moderately fast gas–liquid reaction in which mass transfer and reaction are consecutive processes, often rate determining. The kinetic model^{26–29} was proposed for oxyethylation of various starting materials (alcohols, alkylphenols, and fatty acids) carried out in the presence of a typical alkaline catalyst.³ These authors demonstrated that the oxyethylation of nonylphenol carried out in an autoclave under vigorous mixing (up to 3000 rpm) is controlled by diffusion. The volumetric mass-transfer coefficient amounts to 0.5 s^{-1} at 3000 rpm and is no longer limiting when compared to the intrinsic kinetics at typical reaction conditions. When the kinetic model was used to duplicate the results in a commercial plant with a 10-m^3 stirred reactor, the volumetric mass-transfer coefficient was determined to be only 0.04 s^{-1} , demonstrating that the process was clearly mass-transfer controlled.

The same probably stands for the oxyethylation of fatty acid methyl esters under the conditions studied in this work (the rate of mixing equal to 350 rpm). Thus, the reaction depends on the rate of EO transport to the liquid phase. The delivered EO is immediately consumed in successive parallel reactions:



giving products with various numbers of oxyethylene groups. k_0 , k_1 , k_2 , and k_{n-1} denote the rate constants of

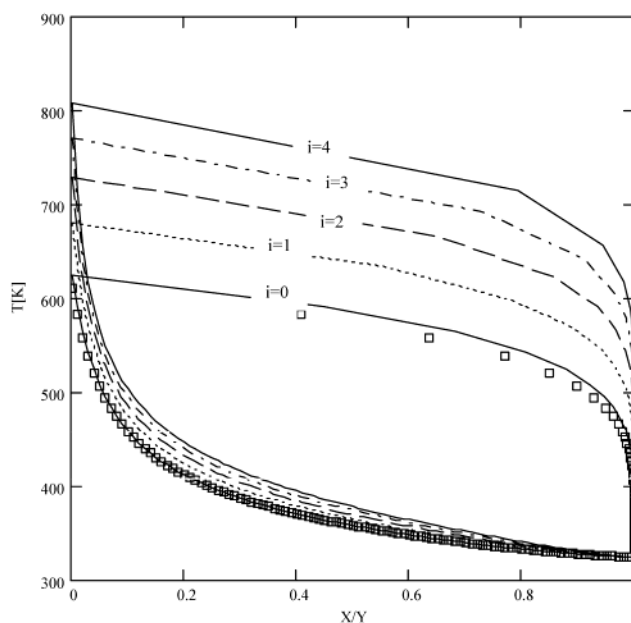


Figure 3. Liquid–vapor equilibrium for binary mixtures of ethylene oxide and methyl dodecanoate ($i = 0$) and its oxyethylated homologues with different numbers of oxyethylene groups ($i = 1–4$).

the first, second, third, and n reaction steps. However, the contribution of the reaction depends on the process temperature and the degree of oxyethylation. An increase of temperature enhances the role of diffusion, while an increase of oxyethylation degree has an opposite effect caused by increased concentration of EO dissolved in the liquid phase. All this means that the computed constants cannot be considered as typical kinetic constants but only as relative estimates of consecutive reaction steps.

The following assumptions can be considered: (1) reactions proceed in the liquid phase (lq) only; (2) concentration of EO in the liquid phase results from vapor–liquid equilibrium and depends on actual degree of oxyethylation; (3) catalyst is nonvolatile and its concentration is constant (catalyst is soluble in the mixture of reactants under reaction conditions); (4) the gas phase contains only EO.

Rates of above consecutive reaction steps (eqs 2) depend on reactant concentrations (the second-order reactions) according to the following relationships:

$$\begin{aligned}
 -dC_{\text{MD}}/dt &= k_0 C_{\text{MD}} C_{\text{EO}} \\
 dC_{\text{MEDO}_1}/dt &= k_0 C_{\text{MD}} C_{\text{EO}} - k_1 C_{\text{MEDO}_1} C_{\text{EO}} \\
 dC_{\text{MEDO}_i}/dt &= k_{i-1} C_{\text{MEDO}_{i-1}} C_{\text{EO}} - k_i C_{\text{MEDO}_i} C_{\text{EO}} \quad (3)
 \end{aligned}$$

where MD denotes methyl dodecanoate and MEDO_i stands for oxyethylated methyl dodecanoate having “ i ” oxyethylene groups. Taking into account small variations of reactant densities (Table 1), constant volume of liquid reaction mixture (v_{q}) is assumed.

The concentration of EO cannot be expressed as a simple function of its conversion because its amount in the liquid phase is a result of vapor–liquid equilibrium.

Figure 3 shows the liquid–vapor equilibrium for binary mixtures of EO and methyl dodecanoates and its homologues having different numbers of oxyethylene

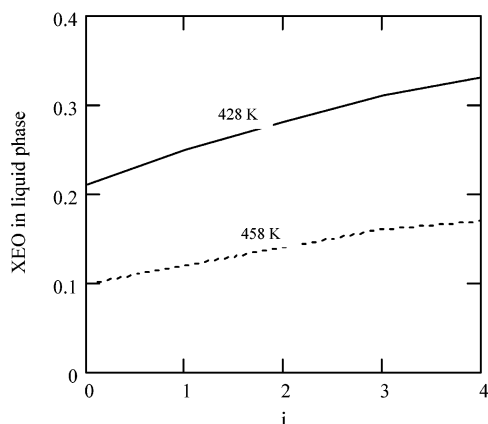


Figure 4. Solubility of ethylene oxide in oxyethylated methyl dodecanoates (MDEO_i) of various hydrophilicity. *i* denotes the number of oxyethylene groups.

groups estimated using the UNIFAC group contribution method to determine the activity coefficients and the Antoine equation to calculate the vapor pressure of EO. In the case of the system containing methyl dodecanoate, the known physicochemical data, such as saturated vapor pressure, could be used. Empty squares in Figure 3 represent the equilibrium estimated from these data. These physicochemical data were also estimated from the molecular structure of methyl dodecanoate using the modified Lydersen method.²⁵ The results are presented in the form of the solid lines. Both approximations have the same character, and the discrepancies are minor. Therefore, the procedure was also used for binary mixtures of EO and successive homologues of oxyethylated methyl dodecanoate. As is seen in Figure 4, the solubility of EO in oxyethylated products increases for each successive homologue. The character of the relationship seems reasonable, as polar EO must be more soluble in a polar environment. Each ethylene group increases the polarity of oxyethylated methyl dodecanoate, but as the next group is introduced to a more polar reagent, the effect becomes smaller.^{30,31} As a result, the polarity of such surfactants increases to a certain asymptote. The same trend is predicted for the solubility data given in Figure 4.

The model for the batch reactor can be formulated as follows:

formation of products:

$$dm_{\text{MDEO}_i}/dt = r_{\text{MDEO}_i} V_{\text{lq}}$$

$$r_{\text{MDEO}_i} = k_{i-1} C_{\text{MDEO}_{i-1}} C_{\text{EO}} - k_i C_{\text{MDEO}_i} C_{\text{EO}} \quad (4)$$

consumption of EO:

$$dm_{\text{EO}}/dt = -r_{\text{EO}} V_{\text{lq}}$$

$$r_{\text{EO}} = \sum_{i=0}^n k_i C_{\text{MDEO}_i} C_{\text{EO}} \quad (5)$$

Because of constant temperature, a heat balance can be omitted.

Table 2. Rate Pseudoconstant of Consecutive Oxyethylation Steps (Degree of Oxyethylation *i* = 0.66) at 428 and 458 K

no. of steps <i>i</i>	k_{428} (dm ³ /mol min)	$C_i =$ k_{i428}/k_{0428}	k_{458} (dm ³ /mol min)	$C_i =$ k_{i458}/k_{0458}
0	0.002	1.0	0.008	1.0
1	0.010	5.0	0.035	5.8
2	0.023	11.5	0.080	13.3
3	0.048	24.0	0.140	23.3
4	0.060	30.0	0.190	31.7
5	0.070	35.0	0.220	36.7
6	0.080	40.0	0.240	40.0

Vapor–liquid equilibrium for the system under moderate pressure can be expressed by the following equations:

$$y_i P = x_i P_i y_i$$

$$\sum y_i = 1, \quad \sum x_i = 1, \quad P_i = f_i(T)$$

$$P = \frac{(m_{\text{EO}})_g RT}{V_g}, \quad v_g = v_r - v_{\text{lq}}$$

$$v_{\text{lq}} = \frac{\sum_{i=0}^n (m_{\text{MDEO}_i})_{\text{lq}} + (m_{\text{EO}})_{\text{lq}}}{\bar{\rho}_{\text{lq}}} \quad (6)$$

where *v* with subscripts r, g, and lq denotes the total volume of reactor and the volume of gas and liquid phases and $\bar{\rho}$ is mean molar density of the reactive mixture.

Integration of the above reactor model versus time lets us obtain time-dependent values of concentrations and pressure inside the reactor. Fitting the experimental profiles of reactor pressure versus time with those obtained from integration by minimizing the square form *F*, where

$$F = \sum_{i=1}^n (P_{\text{exp}}(t_i) - P_{\text{int}}(t_i))^2 \quad (7)$$

let us calculate the reaction rate pseudoconstants presented in Table 2 for the reaction temperatures of 428 and 458 K.

A satisfactory agreement between the measured pressure and that calculated from the model is observed (Figure 5). The results given in Table 2 indicate that rate constants of consecutive steps increase up to the sixth step. The increase of the temperature by 30 °C causes only a 3-fold increase of the rate constants, which supports the important role of EO diffusion from the gas to the liquid phase.

However, it is necessary to point out that the rate constants are somewhat overestimated, as the reaction in the initiation time was totally neglected. Moreover, the computing had to be narrowed to a low degree of oxyethylation (0.66) as the total quantity of EO was introduced entirely at the start of the process.

Compositions of Oxyethylation Products. The main components with various numbers of oxyethylene groups can be easily determined by gas chromatography when pure methyl dodecanoate is used as a starter. However, the method fails for surfactants having a high average molecular weight, i.e., a high degree of oxyethylation, and when the starter contains several esters

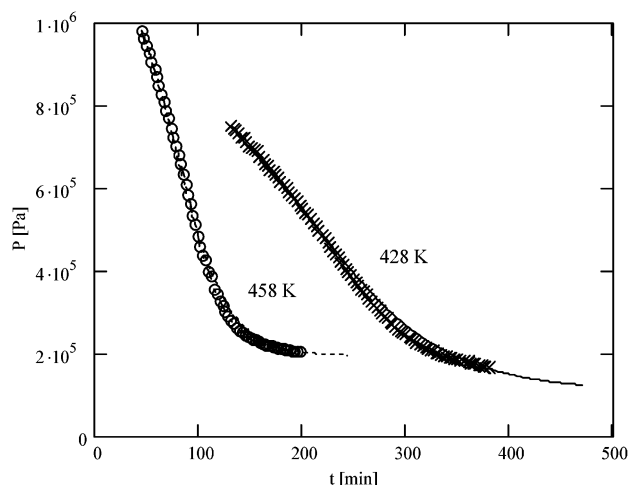


Figure 5. Drop of pressure during oxyethylation of methyl dodecanoate (MD). Solid lines—estimated from the model.

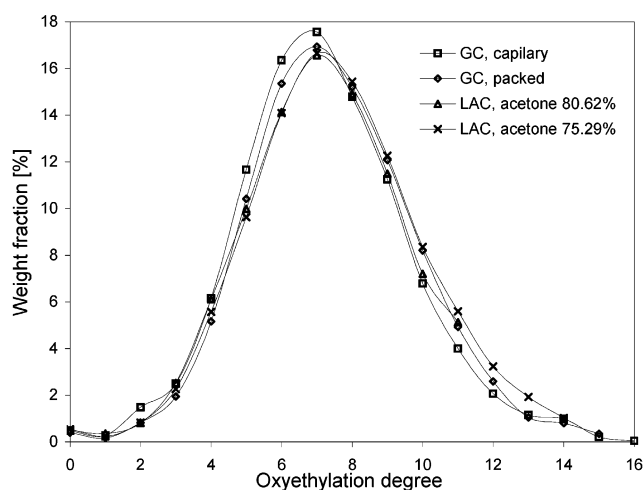


Figure 6. Distribution of homologues as determined by gas chromatography and HPLC.

or alcohols with different numbers of carbon atoms in the alkyl chain. Therefore, GC with packed and capillary columns and HPLC with two different mobile phases were used. As is seen in Figure 6, for example, each analytical technique gives a similar distribution of homologues having different numbers of oxyethylene groups.

The composition of the products depends typically on reaction conditions, including the reagent molar ratio and the catalyst. An increase of the mole ratio of EO to methyl dodecanoate or dodecanol shifts the reaction toward the products having a higher molecular weight and broadens the polyoxyethylene chain distribution.

An important difference in product composition of oxyethylated dodecanol and methyl dodecanoate is observed in the first reaction steps (Figures 7 and 8). The oxyethylated methyl dodecanoates contain less unreacted starter than oxyethylated dodecanol (Table 3). It suggests that the insertion of the first oxyethylene group into methyl dodecanoate is significantly slower than the insertion of the next group(s). The differences disappear when higher homologues having more ($i \geq 4$) ethylene groups are considered (Figure 9).

The rate pseudoconstants estimated from the pressure drop and given in Table 2 can be used to estimate the composition of the oxyethylation products. However, such predictions must be limited to hydrophobic sur-

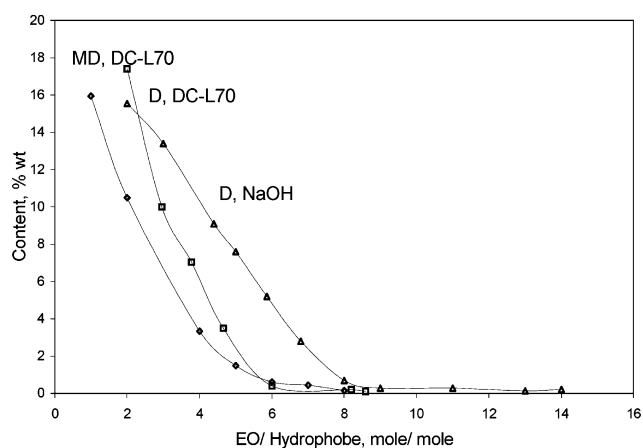


Figure 7. Content of the first homologue having one oxyethylene group in oxyethylated methyl dodecanoate (MDEO₁) and dodecanol (DEO₁) synthesized in the presence of calcium-based catalyst (DC-L70) and NaOH.

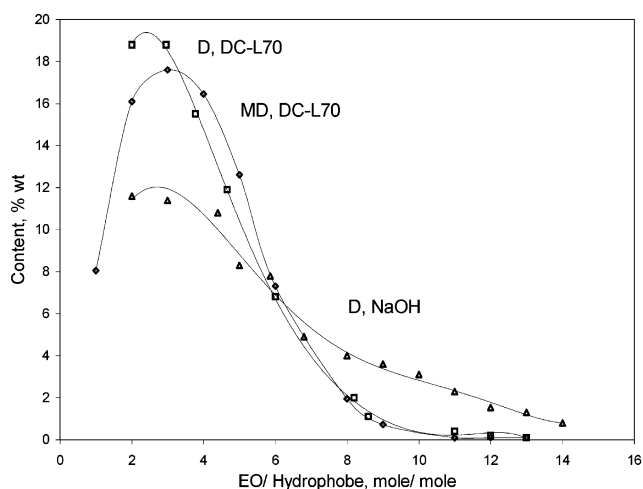


Figure 8. Content of the third homologue having three oxyethylene groups in oxyethylated methyl dodecanoate (MDEO₃) and dodecanol (DEO₃) synthesized in the presence of calcium-based catalyst (DC-L70) and NaOH.

Table 3. Content of Unreacted Methyl Dodecanoate and Dodecanol for Various Average Degrees of Oxyethylation

average degree of oxyethylation	MDEO _i , Ca catalyst		DEO _i	
	GC	HPLC	GC, Ca catalyst	GC, NaOH
1	47.0	41.8	46.8	53.4
2	24.9	18.4	27.4	40.7
3	20.5		15.2	29.2
4	11.3		7.9	22.5
5	4.9	2.1	3.4	16.4
6	1.6	1.2		
7	1.1	1.0		
8	0.4	0.5		

factants of low average degree of oxyethylation. The comparison of the experimentally determined and estimated concentrations (Table 4) can be considered as satisfactory, although significant deviations are observed. The highest discrepancies are observed for the homologue having two oxyethylene groups. The actual conversion of methyl ester is ~20% higher than estimated. It can be explained by neglecting the induction period connected with catalyst dissolution. Thus, the results of chromatography analysis are in satisfactory agreement with the specific rate pseudoconstants esti-

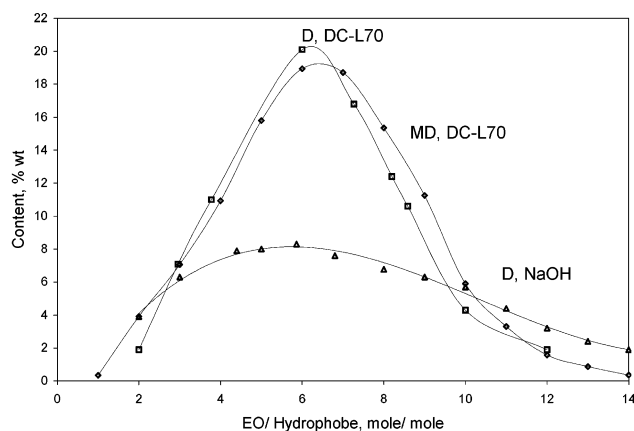


Figure 9. Content of the sixth homologue having six oxyethylene groups in oxyethylated methyl dodecanoate (MDEO₆) and dodecanol (DEO₆) synthesized in the presence of calcium-based catalyst (DC-L70) and NaOH.

Table 4. Comparison of Estimated and Experimentally Determined Concentrations of Oxyethylation Products for the Average Degree of Oxyethylation Equal to 1.1 (Mole Fractions)

homologue	0	1	2	3	4	5	6
X_i^{est}	0.560	0.150	0.140	0.090	0.040	0.016	0.004
X_i^{det}	0.630	0.140	0.060	0.030	0.020	0.017	0.014

Table 5. Distribution Criterion V for Oxyethylated Methyl Dodecanoate (MDEO_{*i*}) and Oxyethylated Dodecanol (DEO_{*i*}) As Determined by Gas Chromatography on a Packed Column^a

average degree of oxyethylation	MDEO _{<i>i</i>} , 185 °C		DEO _{<i>i</i>} , 185 °C		DEO _{<i>i</i>} , 135 °C	
	Ca catalyst	C_{WNG}	Ca catalyst	C_{WNG}	NaOH	C_{WNG}
4	11.7	2.9	10.4	2.6	3.6	3.5
5	16.0	2.3	13.6	2.2	4.2	3.8
6	17.6	1.8	20.0	2.0	4.9	3.7
7	17.7	1.7	19.6	2.6	7.1	5.1
8	17.6	1.7	19.6	0.9	6.4	0.9
9	19.5	1.0	20.8	0.9	6.7	1.0
10	20.5	1.1	21.0	1.1	5.6	1.0
11	23.3	1.9	21.2	1.2	6.7	1.0
12	23.4	2.5	19.2	1.4	7.4	1.2
13	23.6	1.5	23.8	1.3	7.2	1.2
14	24.3	1.7	24.3	-	8.1	1.3

^a Temperature of synthesis: 185 °C for MDEO_{*i*} and 135 and 185 °C for DEO_{*i*}.

Table 6. Distribution Criterion V for Oxyethylated Rape Seed Fatty Acid Methyl Esters Synthesized at Various Temperatures

temperature (°C)	criterion V	
	$i = 10$	$i = 15$
135	9.4	10.4
145	14.2	15.4
155	20.9	19.1
165	22.1	24.9
175	26.1	25.5
185	27.0	26.6

mated from the pressure drop and with the results published recently by Hreczuch.^{32,33}

The products obtained in the presence of calcium-based catalyst have a narrow distribution of the polyoxyethylene chain in comparison to alcohol oxyethylates synthesized in the presence of sodium hydroxide. That difference can be characterized by the distribution criterion V defined by the following equations:³³

Table 7. Szyszkowski Adsorption Coefficients A and B , Correlation Coefficient R , the Maximal Surface Excess at Saturated Interface (Γ_{Max}), and the Free Energy of Adsorption for Oxyethylated Rape Seed Oil Fatty Acid Methyl Esters (MRAEO_{*i*}) (Average Degree of Oxyethylation $i = 10$ and 15) Synthesized at Various Temperatures (from 135 to 185 °C)

surfactant	$A \times 10^8$ (mol/dm ³)	$B \times 10^2$	R	$\Gamma_{\text{max}} \times 10^6$ (mol/m ²)	$-\Delta G_{\text{ads}}$ (kJ/mol)
MRAEO ₁₀ (135 °C)	26.01	10.50	0.993	3.06	37.2
MRAEO ₁₀ (145 °C)	199.2	15.26	0.972	4.39	32.2
MRAEO ₁₀ (155 °C)	456.3	13.94	0.958	4.06	30.16
MRAEO ₁₀ (165 °C)	109.8	14.58	0.986	4.25	33.7
MRAEO ₁₀ (175 °C)	254.2	15.07	0.977	4.39	31.6
MRAEO ₁₀ (185 °C)	68.82	11.62	0.973	3.39	34.8
MRAEO ₁₅ (135 °C)	16.89	8.80	0.992	2.57	38.2
MRAEO ₁₅ (145 °C)	3.40	6.86	0.991	2.00	42.2
MRAEO ₁₅ (155 °C)	92.46	12.2	0.989	3.56	34.1
MRAEO ₁₅ (165 °C)	74.34	12.72	0.995	3.71	34.6
MRAEO ₁₅ (175 °C)	28.82	8.90	0.978	2.59	36.9
MRAEO ₁₅ (185 °C)	16.32	8.82	0.995	2.57	38.3

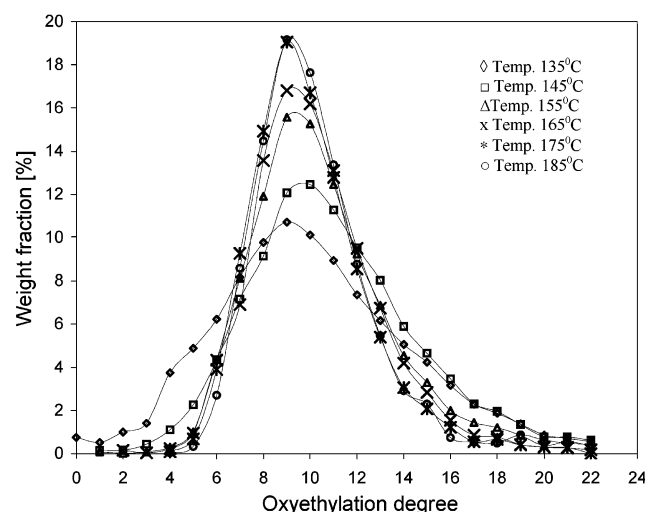


Figure 10. Effect of temperature on homologue distribution in oxyethylated rape seed fatty acid methyl esters for the average degree of oxyethylation equal to 10 (MRAEO₁₀).

$$V = \frac{1}{3 \times 100} \sum_{i=i_{\text{max}}-1}^{i_{\text{max}}+1} w_i^2 i \quad \text{for } i_{\text{max}} > 1 \quad (8)$$

and

$$V = \frac{1}{2 \times 100} \sum_{i=i_{\text{max}}-1}^{i_{\text{max}}+1} w_i^2 i = \frac{w_1^2 + 2w_2^2}{2 \times 100} \quad \text{for } i_{\text{max}} = 1 \quad (9)$$

where i is the degree of polyaddition, w_i is the weight percent of the homologue of average oxyethylation degree equal to i , and i_{max} is the degree of oxyethylation of the main homologue present in the largest quantity.

The distribution can be also characterized by the Weibull–Nycander–Gold distribution parameter C .³⁴ The values of both these parameters are given in Table 5. The results indicate that the considered parameters are not equivalent and change in opposite direction. However, they change in a similar way.

The higher the value of criterion V and the lower the value of parameter C , the more narrow is the distribution of homologues obtained (Table 5). Thus, the more narrow product distribution was obtained with the use of the calcium-based catalyst. The observed effect of the

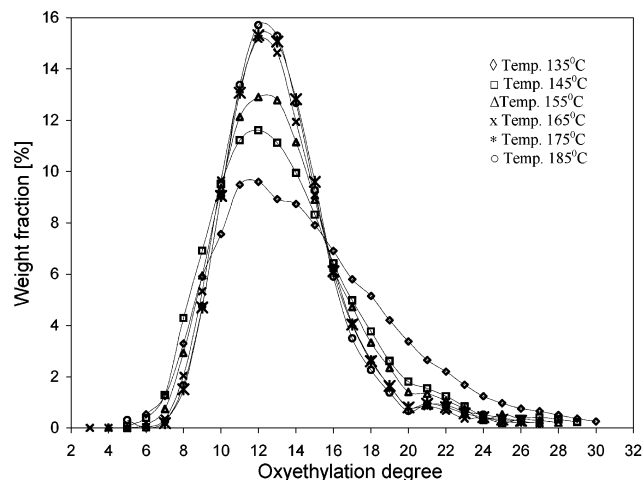


Figure 11. Effect of temperature on homologue distribution in oxyethylated rape seed fatty acid methyl esters for the average degree of oxyethylation equal to 15 (MRAEO₁₅).

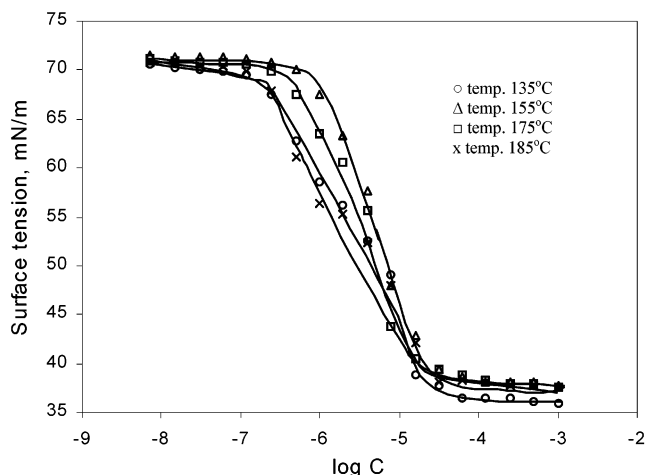
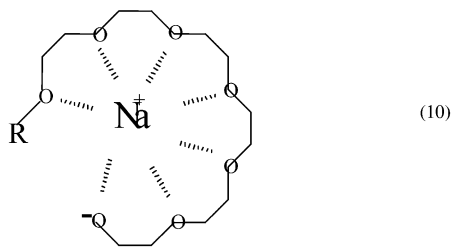
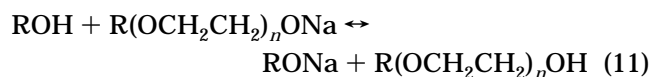


Figure 12. Surface tension isotherms for oxyethylated rape seed fatty acid methyl esters (MRAEO₁₅) synthesized at various temperatures.

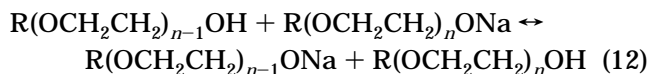
distribution broadening carried out in the presence of monovalent metal cations was explained by additional stabilization of metal oligo(oxyethylene) alkoxides due to the so-called crown effect caused by additional interactions of cation with the free electron pairs on oxygen atoms:



As a result, although the acidity differences between ROH and R(OCH₂CH₂)_nOH are negligible,³ a proton transfer—more strictly, sodium cation transfer reaction—is shifted to the left:



Thus, important amounts of unreacted alcohol are present in the products. That shift is reflected in the value of the equilibrium constant equal to 0.24, as reported by Di Serio et al.²⁶ However, it also means that the reaction



should also be slightly shifted to the left. Actually, this was not observed by Di Serio et al.²⁶ The broadening effect decreases when polyvalent cations are considered, including a calcium-based catalyst.³

Alcohol oxyethylates and methyl dodecanoate oxyethylates were synthesized at different temperatures, typical of these reactions and equal to 135 and 185 °C, respectively. Thus, different compositions could be partly caused by various temperatures.

The compositions of alcohol oxyethylates obtained at various temperatures in the range from 135 to 185 °C do not change when calcium-based catalyst is used.³³

The composition of oxyethylated fatty acid methyl esters depends significantly upon temperature (Figures 10 and 11) and significantly more narrow distributed products are obtained at 185 °C in comparison to those synthesized at 135 °C. It is well reflected in the considerably higher values of criterion V obtained for oxyethylated fatty acid methyl esters at 185 °C (Table 6). All this means is that the distribution of oxyethylated fatty acid methyl esters depends upon both the temperature and the reagent molar ratio. Oxyethylated fatty acid methyl esters become narrow distributed products only at high reaction temperatures and high reagent molar ratios. Their distribution is similar to the distribution of oxyethylated alcohols when the reaction is carried out at 185 °C and for $i = 10$. This phenomenon was studied in more detail elsewhere.³³

Surface Tension Reduction. It was already demonstrated that oxyethylated fatty acid methyl esters effectively decrease both the surface and interfacial tensions. The standard detergent composition shows a washing performance similar to oxyethylated alcohols.^{35–39} Figure 12 shows the typical surface tension isotherms for oxyethylated rapeseed fatty acid methyl esters synthesized at various temperatures. As is seen, the products exhibit similar surface activity. The effect of the polyoxyethylene chain distribution is relatively small and can almost be neglected for such hydrophilic products with the average degree of oxyethylation equal to 10 and 15. As a result, similar values of critical micelle concentration are obtained. They are equal to $(2.7 \pm 0.9) \times 10^{-5}$ and $(3.5 \pm 0.6) \times 10^{-5}$ mol/dm³ (the probability level equal to 0.95) for the average degree of oxyethylation equal to 10 and 15, respectively.

The surface tension isotherms can be well fitted with the Szyszkowski equations (Table 7):

$$\delta = \delta^0[1 - B \ln(1 + C/A)] \quad (13)$$

where δ and δ^0 denote the surface tension for surfactant concentrations equal to C and 0 and A and B are the adsorption coefficients. These constants can be used to estimate the maximal surface excess at saturated

interface Γ_{\max} and the free energy of adsorption:

$$\Gamma_{\max} = B\delta^0/RT \quad (14)$$

$$\Delta G_{\text{ads}} = RT \ln A \quad (15)$$

As is seen in Table 7, the temperature, although it changes the distributions of the polyoxyethylene chain, has a relatively small effect on the values of Γ_{\max} and ΔG_{ads} . As a result, average values can be calculated. They are equal to

$$\Gamma_{\max} = (3.92 \pm 0.45) \times 10^{-6} \text{ mol/m}^2 \quad \text{for } i = 10$$

$$\Gamma_{\max} = (2.83 \pm 0.53) \times 10^{-6} \text{ mol/m}^2 \quad \text{for } i = 15$$

$$-\Delta G_{\text{ads}} = (33.28 \pm 2.01) \text{ kJ/mol} \quad \text{for } i = 10$$

$$-\Delta G_{\text{ads}} = (37.38 \pm 3.36) \text{ kJ/mol} \quad \text{for } i = 15$$

Conclusions

Oxyethylation of fatty acid methyl esters carried out in the presence of calcium-based catalyst gives narrow range distributed products. The distribution depends on temperature, and more narrow products are obtained at higher temperatures. Oxyethylated fatty acid methyl esters contain less unreacted hydrophobic starter than oxyethylated alcohols.

The drop of pressure in the batch process can be satisfactorily modeled, assuming reaction takes place in the liquid phase and estimating the concentration of the EO in the liquid phase from vapor-liquid equilibrium. The modeling supports the important role of EO diffusion from the gas to the liquid phase.

The distribution of the polyoxyethylene chain in hydrophilic oxyethylated fatty acid methyl esters has only a small effect upon the surface tension reduction. However, the temperature affects the slope of adsorption isotherms and the values of adsorption coefficients.

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Nomenclature

A = adsorption coefficient in the Szyszkowski equation
 B = adsorption coefficient in the Szyszkowski equation
 C = concentration
 C_i = reaction rate constant ratio
 ΔG_{ads} = free energy of adsorption
 i = polyaddition degree
 i_{\max} = oxyethylation degree of the main homologue present in the largest quantity
 k_i = rate constant of i th reaction step
 m = number of moles
 M = molecular weight
 P = pressure
 P_c = critical pressure
 P_i = vapor pressure of i th component
 w_i = wt % of the homologue of average oxyethylation degree equal to i
 r = reaction rate of substrate consumption or product formation

R = gas constant

t = time

T = temperature

T_B = boiling point

T_c = critical temperature

V = distribution criterion defined by eq 8

V_g = gas-phase volume

V_{liq} = liquid-phase volume

V_r = total volume of reactor

x = liquid molar fraction

y = vapor molar fraction

Greek Letters

γ = activity coefficient

Γ_{\max} = maximal surface excess at saturated interface

ρ = density

δ = surface tension

Acronyms

D = dodecanol

DEO $_i$ = oxyethylated dodecanol having i oxyethylene groups

EO = ethylene oxide

GC = gas chromatography

HPLC = high-performance liquid chromatography

LAC = liquid adsorption chromatography

MD = methyl dodecanoate

MDEO $_i$ = oxyethylated methyl dodecanoate having i oxyethylene groups

MRA = rape seed fatty acid methyl esters

MRAEO $_i$ = oxyethylated rape seed fatty acid methyl esters having i oxyethylene groups

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