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Role of ethylene oxide solubility in the ethoxylation processes

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Abstract

The role of ethylene oxide solubility in the ethoxylation processes has been studied for what concerns: the influence on the kinetics of the reaction and the behaviour in the different kinds of normally employed reactors, in particular the influence on the reactor instability.

The conclusions of the work are: (i) Henry's law, is a rough and unreliable model to describe ethylene oxide solubilities in a large range of pressures and temperatures, (ii) the predictive UNIFAC model can be applied to a few number of situations, (iii) the employment of NRTL (non random two liquids theory) and Wilson's models seem to be more reliable, but many experimental data are necessary to evaluate the correct parameters of the mentioned models. As it will be seen it is difficult to collect and interpret experimental data. Nevertheless, the precision in the evaluation of ethylene oxide solubilities is fundamental for reactor design, simulation and safety.

1. Introduction

In industry ethoxylation is usually performed in gas–liquid reactors of different types. A first classification of these reactors is possible by considering the dispersed phase. We can have reactors in which gaseous ethylene oxide is bubbled in the liquid phase and others in which liquid is sprayed in an atmosphere of gaseous ethylene oxide. Other possible differences could be the collocation of the heat exchanger inside or outside the reactor and the eventual presence of a stirrer inside the reactor.

The ethoxylation reaction is normally performed in the presence of an alkaline catalyst, usually KOH or NaOH, and a starter. The starter, in the synthesis of nonionic surfactant, could be: a fatty alcohol, an alkyl phenol or a fatty acid, that is, a hydrophobic molecule containing a polar group with an active hydrogen. In the simplest case applicable to the fatty alcohols and the alkyl phenols we can write:

$$\mathrm{MOH+RXH \rightarrow RX^-M^+ + H_2O\uparrow} \quad (1)$$

that is, the catalyst is produced in situ. Then we have the following reactions with ethylene oxide (EO):

$$\mathrm{RX^-M^+ + EO \xrightarrow{k_i} RXEO^-M^+} \quad \text{Initiation} \quad (2)$$

$$\mathrm{RX(EO)_j^-M^+ + EO \xrightarrow{k_p} RX(EO)_{j+1}^-M^+} \quad \text{Propagation} \quad (3)$$

Growing chains are subjected to the following proton transfer equilibria:

$$\mathrm{RX(EO)_j^-M^+ + RXH \rightleftharpoons RX(EO)_jH + RX^-M^+} \quad (4)$$

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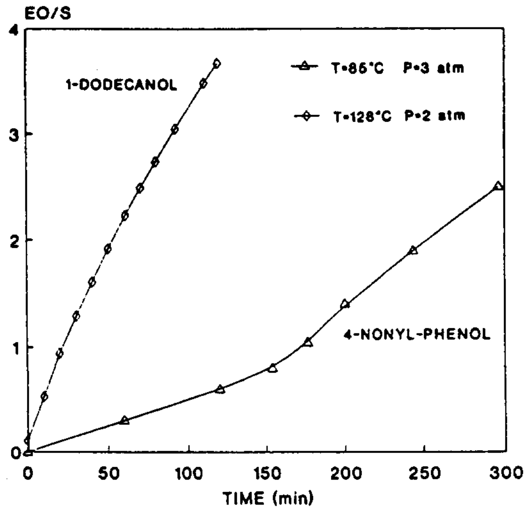

Fig. 1. A comparison of the EO consumption for mole of substrate as a function of time for respectively 1-dodecanol and nonylphenol.

The authors [1–4] observed very different behaviours of the starter alcohols and alkyl phenols in both the activities, and the distribution of oligomers, as a consequence of differences in the anions nucleophilicity, affecting k_i in respect to k_p or in the values of the proton transfer equilibrium constants. As an example, the ethylene oxide consumption as a function of time, for respectively: dodecanol and nonylphenol is reported in Fig. 1. On the contrary, in Fig. 2 is reported a comparison of the oligomer distributions obtained with the two mentioned starters, in correspondence of the same amount of reacted EO.

2. Ethylene oxide solubility and kinetic model

On the basis of the reported reaction mechanism, there has been developed the following kinetic model, valuable for a semibatch reactor:

$$\frac{dm_0}{dt} = -k_i[RX^-M^+][EO]_b \qquad (5)$$

$$\frac{dm_1}{dt} = \{k_i[RX^-M^+] - k_p[RXEO^-M^+]\}[EO]_b \qquad (6)$$

$$\frac{dm_n}{dt} = k_p\{[RX(O)_{j-1}^-M^+] - [RX(EO)_j^-M^+]\}[EO]_b \qquad (7)$$

where $m_0 = [RXH] + [RX^-M^+]$

$= \text{overall substrate concentration} \qquad (8)$

$$m_j = [RX(EO)_jH] + [RX(EO)_j^-M^+] \quad j=1,n \qquad (9)$$

From the mass balance it results:

$$[RX^-M^+] = \frac{m_0B_0}{(m_0+G)} \qquad [RX(EO)_j^-M^+] = \frac{K_{eo_j}B_0m_j}{(m_0+G)} \qquad (10)$$

where:

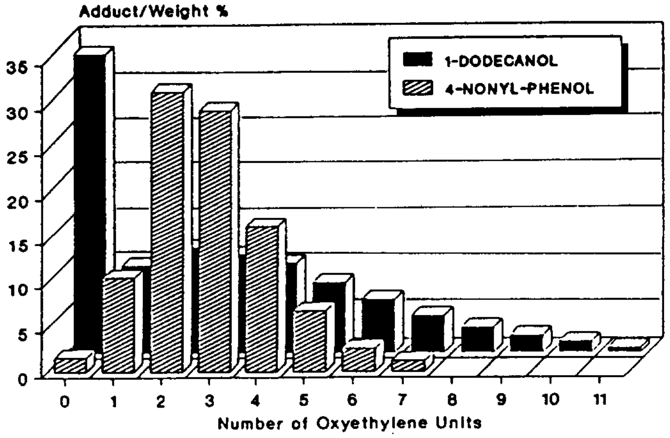

Fig. 2. A comparison of the oligomers distribution obtained for a ratio EO/substrate = 2.7 for respectively 1-dodecanol and nonylphenol.

$$B_0=\sum_{j=0}^{n}[\mathrm{RX(EO)}_j^-\mathrm{M}^+]$$

$$=\text{overall catalyst concentration} \quad (11)$$

$$G=\sum_{j=1}^{n}m_jK_{\mathrm{eo}_j} \quad K_{\mathrm{eo}_j}=\frac{[\mathrm{RXH}][\mathrm{RX(EO)}_j^-\mathrm{M}^+]}{[\mathrm{RX(EO)}_j\mathrm{H}][\mathrm{RX}^-\mathrm{M}^+]} \quad (12)$$

The ethylene oxide consumption could be limited by diffusion, according to the operative conditions. As this is a gas–liquid moderately slow reaction, with a Hatta number $\cong 1$, we can write for the EO consumption:

$$J=\beta_{\mathrm{L}}([\mathrm{EO}]_{\mathrm{i}}-[\mathrm{EO}]_{\mathrm{b}})=[\mathrm{EO}]_{\mathrm{b}}(k_{\mathrm{i}}[\mathrm{RX}^-\mathrm{M}^+] + \mathrm{k}_{\mathrm{p}}\sum_j[\mathrm{RX(EO)}_j\mathrm{O}^-\mathrm{M}^+]) \quad (13)$$

where $[\mathrm{EO}]_{\mathrm{i}}$ is the EO concentration at the gas–liquid interphase, that is the EO solubility, and $[\mathrm{EO}]_{\mathrm{b}}$ the concentration in the bulk. This last results:

$$[\mathrm{EO}]_{\mathrm{b}}=\frac{\beta_{\mathrm{L}}[\mathrm{EO}]_{\mathrm{i}}}{\beta_{\mathrm{L}}+k_{\mathrm{i}}[\mathrm{RX}^-\mathrm{M}^+]+k_{\mathrm{p}}\sum_j[\mathrm{RX(EO)}_j\mathrm{O}^-\mathrm{M}^+]}. \quad (14)$$

Obviously, when diffusion limitations are negligible $[\mathrm{EO}]_{\mathrm{i}} \simeq [\mathrm{EO}]_{\mathrm{b}}$ and $[\mathrm{EO}]_{\mathrm{b}}$ corresponds, in this case, to the ethylene oxide solubility.

The described model is able to simulate the evolution with time of EO consumption, of substrate disappearing and of the distribution of the oligomers, provided that the kinetic and thermodynamic parameters of the model are known. The numerical values of these parameters have been evaluated and reported by Santacesaria et al. in previous papers [1,2]. In those papers EO solubilities have experimentally been determined for each case and interpreted with the very simple Henry's law $H=X_{\mathrm{EO}}/P_{\mathrm{EO}}$, that resulted valid in the experimental field examined. Unfortunately, kinetic runs have been performed at higher temperatures and the extrapolation of the so interpreted solubility data is a rough approximation. Reactor modeling requires often a further extrapolation of both kinetic and solubility parameters. Despite these approximations, we successfully used the model to simulate the performance of different industrial reactors, probably because kinetic parameters and solubilities are strongly correlated and the errors in the calculation of the exact solubility are compensated by the corresponding errors in the kinetic constants. Therefore, in this type of kinetics it is very important to give together with the kinetic parameters the solubility data used for determining them. As a consequence, changing the way for calculating solubilities could require the adjustment of the kinetic parameters if there are differences in the calculated solubilities values. Unfortunately, it is difficult to determine with precision the EO solubilities in such systems that normally are mixtures containing the unreacted substrate and several ethoxylated oligomers containing different number of adducts. In the collection of data these mixtures are normally considered as a unique component with an average number of EO adducts. A small reactivity of nonylphenol, also in the absence of the alkaline catalyst, is another problem in the experimental measurement of the solubilities [5]. These aspects well explain the lack of EO solubility data in such systems. The elaboration of the experimental data is difficult, too, because mixtures of EO with many other components, the oligomers, are normally treated as binary mixtures. Moreover, EO is a small molecule, while, the ethoxylated oligomers are moderately large and have the peculiar structure of the surfactants, that is molecules containing both the polar and the apolar groups and having the tendency to give structured liquids. These situations are the worst to be represented with the usual models applicable to the description of vapour liquid equilibria such as: UNIQUAC, NRTL, Wilson etc. The predictive method UNIFAC, for example, gives poor results, in particular for nonylphenol and derivatives for which we found mean errors greater than 30%. From the results of our preliminary studies the performances of the NRTL and Wilson methods are better, giving mean errors less than 10%.

In Table 1 the EO solubilities in ethoxylated nonylphenol, containing a mean value of 9 EO adducts and the performances obtained respectively with UNIFAC, NRTL and Wilson, are reported as an example. In Table 2 are reported similar data for dodecanol +4.3 EO adducts. Many other experimental data are necessary to confirm these conclusions, remembering that if solubility data change, kinetic parameters must be adjusted consequently to give the same values of reaction rates.

Table 1
Examples of EO solubility equilibrium data at different temperatures [5] and the comparison of the performances obtained with UNIFAC, NRTL and Wilson models to describe EO solubility in ethoxylated nonylphenol with EO to substrate ratio equal to 9. Mean errors have been determined on many other data

x_{EO}	P_{EO} (atm)			Mean error %		
	90°C	110°C	130°C	UNIFAC	Wilson	NRTL
0.240	0.99	1.41	1.97			
0.514	2.82	3.95	5.55	33	6	5
0.700	4.93	7.05	9.87			
0.774	6.06	9.16	12.69			

Table 2
Examples of EO solubility equilibrium data at different temperatures and the comparison of the performances obtained with UNIFAC, NRTL and Wilson models to describe EO solubility in ethoxylated dodecanol with EO to substrate ratio equal to 4.3. Mean errors have been determined on many other data

x_{EO}	P_{EO} (atm)			Mean error %		
	70°C	99°C	150°C	UNIFAC	Wilson	NRTL
0.094	–	–	0.72			
0.102	–	0.40	–			
0.134	0.43	–	–			
0.154	–	–	1.03			
0.187	–	0.73	–			
0.203	–	–	1.38	35	16	20
0.237	0.64	–	–			
0.248	–	–	1.70			
0.259	–	1.00	–			
0.287	–	–	2.08			
0.300	–	1.20	–			
0.317	0.89	–	–			

3. Ethylene oxyde solubility and reactors behaviour

As mentioned in a previous section we distinguish two types of reactors: those having gaseous EO as dispersed phase and those in which the liquid is sprayed in the EO continuous phase. In both cases EO must be transferred from the gas to the liquid phase, before the occurrence of the reaction, but in the case in which liquid is the dispersed phase mass transfer and reactions occur in two different parts of the reactor, as shown in Fig. 3. Liquid drops are filled with EO until the solubility equilibrium is reached, if obviously the drops are small and flight times are long enough. The drops saturated with EO fall on the liquid surface, at the top of the reactor. Here we have, therefore, an EO saturated layer that begins to react and moves toward the bottom of the reactor. By assuming, as a reasonable approximation, a plug flow behaviour, the EO concentration profile along the liquid column can be easily calculated together with the temperature profile by integrating the following equations from the top to the bottom of the liquid column:

$$\frac{d[EO]}{dz}=\frac{A[EO]}{Q_L}\left(k_i[RX^-M^+]+k_p\sum_j[RX(EO)_jO^-M^+]\right) \qquad (15)$$

$$\frac{dT}{dz}=\frac{\Delta H_R}{C_P\rho}\frac{d[EO]}{dz} \qquad (16)$$

where A = cross-section of the reactor, Q_L = recirculating feed rate of the liquid, z = distance from the top of the reactor, C_P = specific heat, ρ = density.

In this case a correct evaluation of the EO solubility allows to define more reliable profiles, the total amount of EO present in the reactor and the pressure in the gaseous phase. Some complications arise when drops are not completely saturated or when the recirculating liquid contains residual unreacted EO. In these cases we must evaluate the amount of EO entering in a drop, of a mean size, during an averaged flight time. The mean EO concentration in the drop can be calcu-

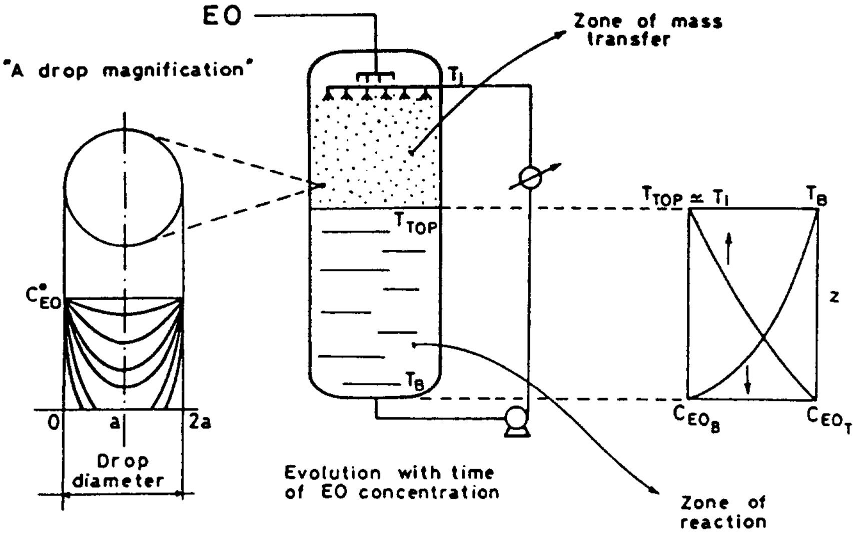

Fig. 3. Scheme of a reactor in which liquid phase is sprayed into the EO gaseous atmosphere.

lated by integrating the equation related to the diffusion in a sphere:

$$\frac{\partial C}{\partial t}=D\left[\frac{\partial^2 C}{\partial r^2}+\frac{2}{r}\frac{\partial C}{\partial r}\right] \tag{17}$$

with the initial condition

$$C(r,0)=\bar{C}(r)=C_i$$

and boundary conditions

$$C(a,t)=\bar{\bar{C}}(t)=C_0 \qquad \left.\frac{\partial C}{\partial t}\right|_{r=0}=0$$

where a = drop radius, C_i = EO initial concentration, C_0 = EO surface concentration, r = distance from the drop center, t = flight time, D = diffusion coefficient.

The analytical solution of this equation has been given by Crank [6].

It is clear that correct values of EO solubilities allow reliable calculations for modeling or simulating both the mass transfer and reaction zone of the reactor. In the case of reactors where gaseous EO is dispersed in the well-mixed liquid phase, the performances of the reactor can be described with the Eqs. (5–14), already seen in the previous

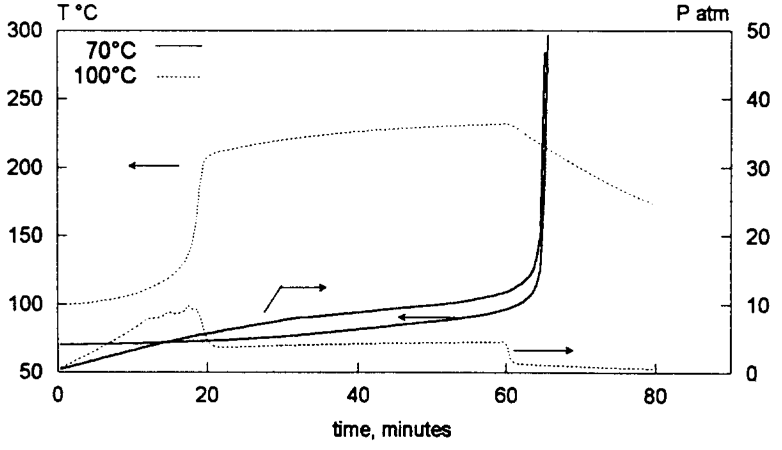

Fig. 4. Evolution of the pressure and temperature with time in a well-mixed reactor for different temperatures at which is kept the fluid of the heat exchanger used both for heating and cooling the reaction mixture (nonylphenol). EO feed rate is interrupted for pressures greater than 8 atm. The catalyst (KOH) concentration has been taken 0.38% in weight.

section, and the importance of EO solubility has already been stressed.

Another aspect that is worth to be mentioned is related to the observation that, at low temperature, EO equilibrium concentrations strongly increase. It is easy to demonstrate, by calculation, that if a well-mixed reactor is loaded with EO, at low temperature (70–80°C), runaway is possible also in the presence of an efficient heat exchanger.

An example of this type of calculations is reported in Fig. 4. This behaviour is in agreement with the observed accidents occurred for the explosion of EO cylinders [7]. That is, very high EO concentrations are dangerous in the presence of traces of a polymerization catalyst. It is possible, knowing the efficiency of the heat exchanger, to evaluate a critical concentration of EO over which the runaway could occur at a given temperature and pressure.

To conclude we have shown the importance of the availability of precise EO solubility data for the liquid mixtures that are present in an ethoxylation reactor in order to: (i) collect reliable kinetic data, (ii) model and simulate the ethoxylation reactor and (iii) predict instability of these reactors.

4. List of symbols

B_0	catalyst concentration (mol/cm^3)
H	partition coefficient for ethylene oxide (1/atm)
J	mass-transfer rate (mol/(cm^3 s))
k_i	constant rate of initiation (cm^3/(mol s))
k_p	constant rate of propagation (cm^3/(mol s))
K_{eoj}	equilibrium constants of proton-exchange reaction
P_{EO}	ethylene oxide partial pressure (atm)
X_{EO}	molar fraction of ethylene oxide
β_L	overall gas–liquid mass-transfer coefficient (1/s)
ΔH_R	reaction enthalpy
$[EO]_i$	ethylene oxide interface concentration (mol/cm^3)
$[EO]_b$	ethylene oxide bulk concentration (mol/cm^3)
$[RXH]$	substrate concentration (mol/cm^3)
$[RX(EO)_jH]$	oligomer concentration with j EO adducts in the chain (mol/cm^3)
$[RX^-M^+]$	charged substrate concentration (mol/cm^3)
$[RX(EO)_j^-M^+]$	charged oligomer concentration with j EO adducts in the chain (mol/cm^3)

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