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POLY(ETHYLENE GLYCOL)-NONYLPHENYL ETHER EXTRACTION WITH SUPERCRITICAL CARBON DIOXIDE IN A PACKED COLUMN

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ABSTRACT

A semibatch extraction of poly(ethylene glycol)nonylphenyl ether (PEG-NPE) with supercritical carbon dioxide was studied at 20,0 MPa, and 323 K. The process was carried out in a stainless steel column, filled with inert packing, wetted by the polymer. Three representative polymer fractions (degree of polymerisation 40, 50, and 60) and the total polymer amount at the column exit were monitored for a period of 4 h. Experimental data obtained were used for evaluation of process parameters, applying a model that

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considers the mass transfer on both phases and the longitudinal mixing in the solvent-rich phase, continuously flowing through the packed column.

It was found that for the studied conditions the longitudinal mixing is very pronounced, but the active contact area is strongly reduced, supposedly as a result of solvent-rich phase channeling. After the transient initial period, the overall mass-transfer coefficient is controlled by the component diffusivity in the polymer-rich phase.

Key Words: Supercritical fluid extraction; Packed column; Poly (ethylene glycol)s; Mass transfer; Mathematical model

INTRODUCTION

Poly(ethylene glycol)s (PEG) are synthetic polymers, which depending on their average molar mass and composition, are used in pharmaceutical and cosmetic industries. Recently, their extraction and fractionation by supercritical fluids was subject of several studies (1–3). A special interest among PEGs represents the poly(ethylene glycol)nonylphenyl ether (PEG-NPE). Its molecule has balanced hydrophobic and hydrophilic parts, which determines its attractive surface active properties. Some data about the solubility of this polymer in supercritical carbon dioxide were also reported (4).

The mechanism of mass transfer in the gas-liquid and liquid-liquid systems in the packed columns is well known (5–9). However, until now only few data on the kinetics of supercritical extraction in packed columns are available (10–13). Most of these studies considered supercritical carbon dioxide extraction of various species from their aqueous solutions. The columns were usually described and modelled as bubble columns—the authors studied the mass transfer between CO_2 bubbles and surrounding aqueous solution (14).

In this study the liquified PEG-NPE was subject of semibatch continuous flow extraction with supercritical carbon dioxide in a packed column.

EXPERIMENTAL

A commercial PEG-NPE (polyoxyethylene α-nonyl-*para*phenylene ω-hydroxyl) with general formula $C_9H_{19}\text{-}C_6H_4(OCH_2CH_2)_n\text{-}OH$ and an average molar mass of 2500 g/mol, supplied by Fluka under the trade name Synperonic NP 30, was used in the experiments. Under the experimental conditions (temperature of 323 K and pressure of 20,0 MPa) the polymer is viscous liquid. At the mentioned experimental conditions viscosity of liquified and CO_2

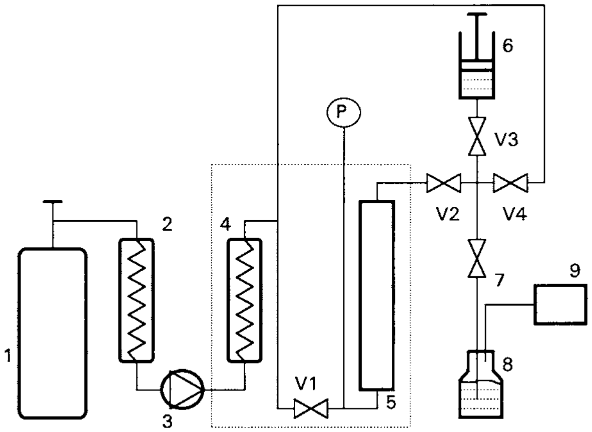

Figure 1. Experimental set-up: (1) solvent tank, (2) solvent cooler, (3) high pressure pump, (4) solvent preheater, (5) packed extraction column, (6) syringe, (7) micrometric valve, (8) recuperation vessel, and (9) gas meter.

saturated poly(ethylene glycol)nonylphenyl ether is 0,57 Pa · s as reported earlier (15).

The experimental set-up used for semibatch extraction of PEG-NPE is shown in Figure 1. The main part of this arrangement is the extractor 5—a stainless steel tube 16 mm i.d. and 300 mm long, filled with uniform glass spheres of 3,2 mm diameter and void fraction 0,42. The packing surface is covered with a thin film of liquified polymer, of average thickness estimated to be $1{,}95 \cdot 10^{-5}$ m. After system loading with heated and pressurized carbon dioxide and after reaching the desired pressure and system stabilization, valves *V2* and *7* are opened. The solvent passes through the column with a controlled flow rate. The extraction process is carried out at a constant temperature, mentained with a precision of 0,1 K. The bypassing line with the valve *V4* serves to load the circuit portion after the column exit with a fresh carbon dioxide to avoid the drastic pressure drop when one oppens the valve *V2*.

The leaving fluid, containing the dissolved polymer, is depressurised to atmospheric pressure in the recuperation vessel *8*, which contains ethanol. Extracted polymer remains in the vessel, and the released carbon dioxide leaves the system. An additional amount of ethanol, supplied by the syringe *6*, provides a total polymer washout and recuperation. The amount of extracted polymer after ethanol evaporation, was determined gravimetrically and its mass distribution—by a size exclusion chromatography, using a differential refractometer “Waters 410.” The latter was equiped with two Styragel® columns “Polymer Laboratories”—100 Å and 500 Å (300 × 7,5) and a HPLC pump “Waters 510.” Calibration was made by

PMMA strandards. The mobile phase was tetrahydrofurane pumped with a flow rate of 1,0 ml/min.

EXTRACTION PROCESS MODEL

In order to symplify the mathematical description of the extraction process, the column is presented as a prism with a rectangular cross section. The ratio between the free cross section and the one occupied by the polymer was the same as the ratio in the real device ignoring the presence of the inert glass beads. The contact area between the two phases per unit lenght was also the same.

The mass balance equation for the i-th polymer component in the solvent-rich phase is given by:

$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial z} + D_{L,i}\frac{\partial^2 C_i}{\partial z^2} + \frac{1-\varepsilon}{\varepsilon}k_{f,i} \cdot a(C_i - m_i \cdot Cp_i) \tag{1}$$

whereas its diffusion through the polymer layer, covering the glass beads, is described by the second Fick's law:

$$\frac{\partial Cp_i}{\partial t} = D_{P,i}\frac{\partial^2 Cp_i}{\partial y^2} \tag{2}$$

The first right-hand side term in Equation 1 represents the specie convective transport in the solvent-rich phase, the second one its longitudinal mixing in the same solution, while the third gives the mass exchange flux between the two phases.

The initial and boundary conditions are:

$$t = 0 \quad (\forall z) \qquad C_i = C_i^* \tag{3}$$

$$z = 0 \quad (\forall t) \qquad C_i = 0 \tag{4}$$

$$z = L \quad (\forall t) \qquad \frac{\partial C_i}{\partial z} = 0 \tag{5}$$

$$y = 0 \quad (\forall z, t = 0) \qquad Cp = Cp^0 \tag{6}$$

$$y = H \quad (\forall z, \forall t) \qquad D_{P,i}\frac{\partial Cp_i}{\partial y} = k_{f,i}(C_i - m_i \cdot Cp_i) \tag{7}$$

Equation (7) stems from the equallity between the two i-th component fluxes: the one leaving the polymer-rich phase surface and the one entering into the solvent phase.

RESULTS AND DISCUSSION

As already mentioned PEG-NPE extraction process was studied at 20,0 MPa, 323 K, and flow rate of supercritical carbon dioxide of 1,0 to 3,0 ml/min. The

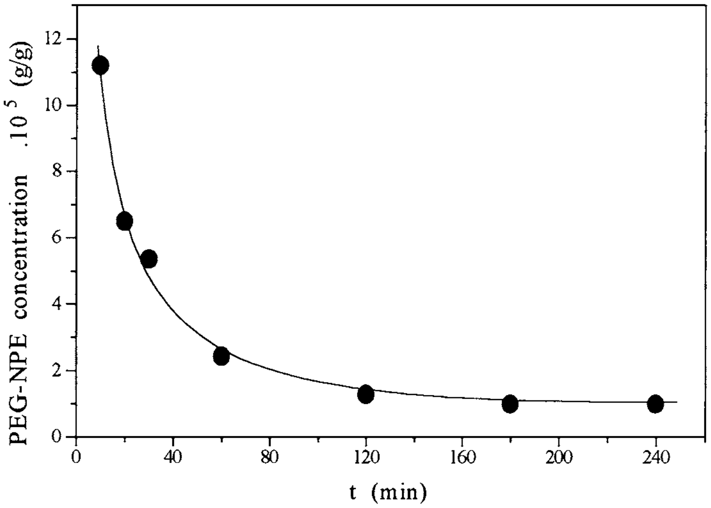

Figure 2. Evolution of total PEG-NPE concentration in the leaving solvent ($Q = 1{,}5$ ml/min).

evolution of total polymer concentration, measured at the column exit at a flow rate of 1,5 ml/min is shown in Figure 2. In the beginning, the polymer concentration is close to the equilibrium one, previously reported (4). During the first 2 h, as a result of continuous washout of the saturated solvent, the solute concentration at the exit decreases, which corresponds to a transition regime. After this period, the concentration becomes relatively stable, corresponding to the established regime of dynamic equilibrium. Figure 3 shows the effect of solvent flow rate on polymer concentration at the column exit during the regime of dynamic equilibrium. The concentration decreases with rise of the flow rate because of diminution of the solvent-rich phase mean residence time, although the increase of the polymer yields with the flow rate. An increase of the solvent flow rate above 2,5 ml/min deteriorates the extraction process due to foam formation resulting in a nondissolved polymer entrainement out of the column.

In order to identify the parameters involved in the model, Equations (1–7) were solved by a finite difference technique applying an explicite approximation scheme. In this way the concentrations of three selected components representing polymer molecules of degree of polymerisation: $i = 40$, $i = 50$ and $i = 60$, respectively, in both phases were obtained by means of the dynamic simulator TUTSIM® (Meerman Automation). The values of these parameters, namely the specific contact area a, i-th component diffusivity in the polymer-rich phase $D_{P,i}$, its longitudinal mixing coefficient $D_{L,i}$, and mass-transfer coefficient in the solvent-rich

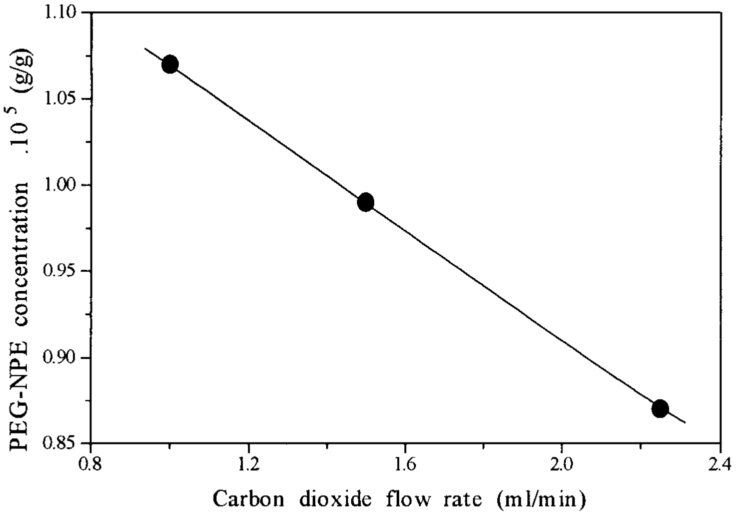

Figure 3. Effect of solvent flow rate on the total PEG-NPE concentration in the solvent-rich phase (steady-state regime).

phase $k_{f,i}$, were evaluated applying the incorporated simplex optimisation method of Nedler and Mead (16). These values are presented in the Table 1.

The curves shown in Figure 4 represent the best fit simulated concentrations for the studied PEG-NPE components, calculated on the base of described mathematical model, and the experimental results, represented by the circles.

An analysis of the results obtained shows that the longitudinal mixing coefficients $D_{L,i}$ increase slightly when the polymer molar mass increases, while the mass transfer coefficients $k_{f,i}$ decrease in a more pronounced manner, because of the hampered mobility of the larger molecules.

The mass-transfer coefficients $k_{f,i}$ obtained by this model were compared to the coefficients calculated on the bases of two correlations largely empolyed for liquids and supercritical solutions. For the values of Re in the interval: $3 < Re < 10^4$ (in our case: $u = 3{,}85 \cdot 10^{-4}$ m/s, $Re = 14{,}43$), Wakao and Kaguei proposed the

Table 1. Evaluated Model Parameters for Specified PEG-NPE Components

i	Molar Mass [g/mol]	$k_{f,i}$ [m/s]	$D_{L,i}$ [m^2/s]	$D_{P,i}$ [m^2/s]	a [m^2/m^3]
40	1980	$1{,}32 \cdot 10^{-5}$	$5{,}07 \cdot 10^{-6}$	$7{,}54 \cdot 10^{-15}$	476
50	2420	$1{,}19 \cdot 10^{-5}$	$5{,}13 \cdot 10^{-6}$	$3{,}50 \cdot 10^{-15}$	476
60	2860	$1{,}07 \cdot 10^{-5}$	$5{,}18 \cdot 10^{-6}$	$1{,}61 \cdot 10^{-15}$	476

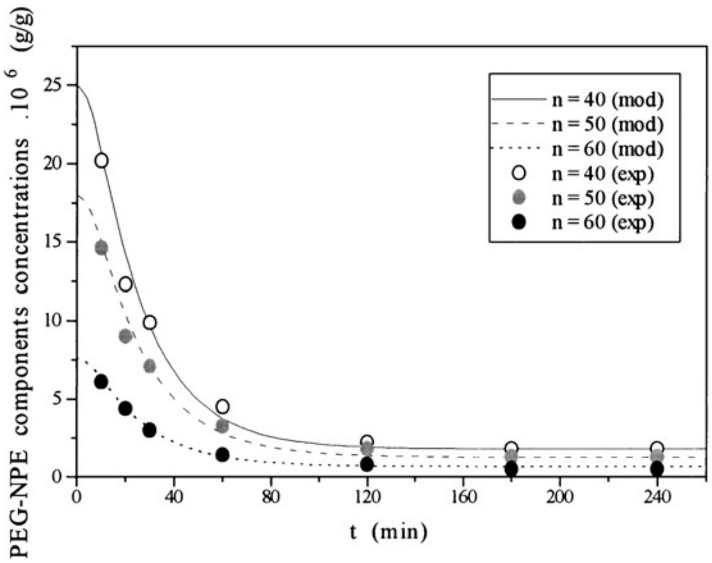

Figure 4. Concentrations of the three PEG-NPE components in the leaving solvent: the symbols are the experimental points and the curves—computed best fit results.

following correlation (17):

$$Sh = 2 + 1{,}1 \cdot Sc^{0{,}333} \cdot Re^{0{,}6} \tag{8}$$

The solute diffusivities in the solvent-rich phase, necessary for calculation of $k_{f,i}$ were obtained by the method of Wilke (18). Sassiat et al. demonstrated that this method proposed for ordinary liquids is also valid for supercritical fluids (19).

Summarizing a large number of results obtained by various authors on the mass transfer in gases and liquids in packed columns, Sherwood et al. proposed a correlation, valid both for gases and liquids in the interval $10 < Re < 2500$ (20):

$$\frac{k_f}{u} Sc^{0{,}667} = 1{,}17 \cdot Re^{-0{,}415} \tag{9}$$

Because the properties of the supercritical fluids are intermediate between those of the liquids and the gases, correlation (9) is also suitable for determination of solute diffusivity in a supercritical medium.

Table 2 compares the mass-transfer coefficients obtained applying the proposed model to the coefficients calculated on the bases of the correlations proposed by Sherwood et al. (20) and by Wakao and Kaguei (17). One can notice that there is a good agreement between the results obtained by using different methods.

The longitudinal mixing coefficients were also calculated independently using the correlation proposed by Tan and Liou (21), describing the axial dispersion

Table 2. Comparison of Mass-Transfer Coefficients Evaluated from This Model and Calculated Using the Correlations Proposed by Sherwood et al. and by Wakao and Kaguei

	k_f [m/s]		
Degree of Polymerization	Calculated According Wakao and Kaguei (17)	Calculated According Sherwood et al. (20)	Evaluated from This Model
40	$1{,}42 \cdot 10^{-5}$	$1{,}08 \cdot 10^{-5}$	$1{,}32 \cdot 10^{-5}$
50	$1{,}31 \cdot 10^{-5}$	$0{,}99 \cdot 10^{-5}$	$1{,}19 \cdot 10^{-5}$
60	$1{,}22 \cdot 10^{-5}$	$0{,}93 \cdot 10^{-5}$	$1{,}07 \cdot 10^{-5}$

of a solute in supercritical carbon dioxide in packed beds:

$$Pe = 1{,}634 \cdot Re^{0{,}265} \cdot Sc^{-0{,}919} \tag{10}$$

The values of these coefficients obtained, applying our model (Tab. 1) are close to the values calculated using the correlation of Tan and Liou. For macromolecules with polymerization degree of 40, 50, and 60 they are: $5{,}31 \cdot 10^{-6}$, $5{,}92 \cdot 10^{-6}$, and $6{,}44 \cdot 10^{-6}$ m/s, respectively. In fact, most of the authors estimate that the axial dispersion is constant for different solutes in the same medium, considering the phenomenon as purely hydrodynamic and macroscopic. However, Edwards and Richardson (22) have shown that at very low flow velocities the axial dispersion is closely related to the molecular diffusion and the axial dispersion coefficient is a function of the solute diffusivity. The correlation proposed by Tan and Liou take into account this dependence. In our case, the role of molecular diffusion is significant because of the low solvent flow rate, but the contribution of the eddy diffusivity should not be neglected, too, that could explain the smaller difference between the coefficients evaluated by this model for the molecules of different polymerisation degree.

The specific contact surface, evaluated from the model (Eqs. (1) to (7)) was $a = 476$ m^2/m^3, a value representing only 1/5 of the value of this parameter, assuming that the total packing surface is active. Obviously, as a result of a formation of channels and stagnant zones, the supercritical fluid passing through the column is not in effective contact with the polymer on the whole available packing area. This is confirmed by the fact that the transient, washout period is quite long due to a pronounced fluid intermixing and channelling. The diffusion coefficients of the PEG-NPE components in the polymer-rich phase decrease when their size increases. The values for $D_{P,i}$ are almost one order of magnitude lower than the auto diffusion coefficients of PEG-15000 obtained by Tanner (23) and Squirda (24). This could be explained by the difference in polymer structure.

It was found that the model is very sensitive with respect to the variation of parameters $D_{L,i}$, $D_{P,i}$, and a, and less sensitive to $k_{f,i}$.

CONCLUSION

A semibatch extraction process of PEG-NPE with supercritical carbon dioxide in a packed bed column was studied. It was observed that the total polymer concentration decreases with a solvent flow rate, while its yield increases. A model of the extraction process was proposed. On the basis of the experimental results and the model, the process parameters (longitudinal mixing and mass-transfer coefficients in the solvent-rich phase, diffusion coefficients in the polymer-rich phase, and effective specific area) for some PEG-NPE components were obtained. It was observed that the longitudinal mixing coefficients increase slightly with the molar mass of polymer, whereas the mass transfer coefficients in the solvent-rich phase and the diffusion coefficients in the polymer-rich phase decrease because of the reduced mobility of the larger molecules. As a result of fluid channelling and longitudinal dispersion, the active contact area between phases is strongly reduced and the flow regime is far from the ideal plug-flow regime.

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SYMBOLS

a	specific area [m^2/m^3]
C_i	concentration of the i-th polymer component in the solvent-rich phase [g/g]
C_i^*	equilibrium concentration of the i-th component in the solvent-rich phase [g/g]
Cp_i	concentration of the i-th component in the polymer-rich phase [g/g]
Cp_i^o	initial concentration of the i-th component in the polymer-rich phase [g/g]
$D_{L,i}$	longitudinal dispersion coefficient [m^2/s]
$D_{P,i}$	diffusion coefficient in the polymer-rich phase [m^2/s]
$D_{S,i}$	diffusion coefficient in the solvent-rich phase [m^2/s]
d_p	particle size [m]
H	thickness of the polymer-rich phase [m]
i	polymer degree
$k_{f,i}$	mass-transfer coefficient in the solvent-rich phase [m/s]
L	column length [m]

m_i	partition coefficient
Q	solvent flow rate [kg/s]
t	time [s]
u	solvent velocity [m/s]
y	direction normal to the contact interface
z	direction of solvent flow
ε	volume fraction of the solvent-rich phase
μ	fluid viscosity [Pa · s]
ρ	fluid density [kg/m^3]
Pe	Peclet number, $d_p \cdot u/D_{L,i}$
Re	Reynolds number, $d_p \cdot u \cdot \rho/\mu$
Sc	Schmidt number, $\mu/(\rho \cdot D_{S,i})$
Sh	Sherwood number, $d_p \cdot k_{f,i}/D_{S,i}$

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