*J. Chem. Eng. Data* **2009,** *54,* 1551–1559

# Modeling the Phase Behavior of PEO−PPO−PEO Surfactants in Carbon Dioxide Using the PC-SAFT Equation of State: Application to Dry Decontamination of Solid Substrates[†]

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The phase behavior of several commercially available poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) block copolymers (PEO−PPO−PEO or Pluronics L) in compressed carbon dioxide has been investigated within the framework of dry nuclear decontamination. For this purpose, cloud points have been measured in the pressure and temperature range from $P = (10 \text{ to } 40)$ MPa and from $T = (293 \text{ to } 338)$ K, respectively. To find a reliable method for surfactant selection, the perturbed-chain statistical association fluid theory (PC-SAFT) equation of state (EoS) has been applied to model the experimental data. The pure-component and the respective homopolymer + $CO_2$ binary interaction parameters have been fitted to liquid densities and to homopolymer + $CO_2$ binary equilibrium data. The phase behavior of Pluronics L copolymers as a function of concentration, molar mass, and copolymer composition has been predicted very accurately using a constant PEO−PPO binary interaction parameter $k_{\text{PEO-PPO}} = 0.007$. The PC-SAFT model was also successfully applied to Pluronics R copolymers (PPO—PEO—PPO), although a different $k_{\text{PEO-PPO}} = -0.018$ was required to match the experimental data. The model predictions have shown that Pluronics L copolymers with molar mass $M < 2750 \text{ g·mol}^{-1}$ and a PEO mass fraction in the copolymer of less than 30 % have sufficiently low cloud-point pressures and are therefore the most suitable for the decontamination process.

## Introduction

At present, the low and very-low-activity nuclear wastes (LANW and VLANW) represent 90 % of the total waste volume generated by the nuclear industry in the world. These wastes include different types of solid substrates (e.g., gloves, tissues, soils, hardware. etc.) which have been in contact with radioactive metals, oxides, or ions. Various chemical decontamination techniques are applied to reduce the waste volume and to recover the radioactive contaminants. These techniques are either based on the dissolution of the radioactive contamination in various inorganic acid/chelating agent solutions or on the dispersion of the contaminant in aqueous media using different soluble wetting, dispersing, and/or foaming surfactants.[1,2] Unfortunately, almost all of these techniques are economically unfavorable because they generate a large amount of contaminated secondary liquid wastes. As the environmental and radioactive waste storage management regulations are reinforced, supercritical $CO_2$ ($scCO_2$) ($T_c = 304.12$ K, $P_c = 7.38$ MPa) has gained considerable attention in nuclear decontamination.[3–7] $ScCO_2$ is an attractive alternative to aqueous and organic solvents because it is nontoxic, nonflammable, and inexpensive. However, because of its very low dielectric constant ($\varepsilon = 1.40$ at 15 MPa and 323 K)[8] and low polarizability per volume ($\alpha/v = 2.913 \cdot 10^{-24}$ cm$^3$),[9] $CO_2$ is a poor solvent for water and most polar organic or inorganic compounds. To overcome the polarity difference between the polar compounds and the nonpolar $CO_2$, additives must be used. In the last ten years, the use of specific chelating agents,[10–12] cosolvents,[13] and surfactants[14–19] has been largely studied.

Each type of additive has its own advantages. Chelating agents, for example, can be selected to extract a specific contaminant. In contrast, cosolvents are much more universal. If a polar cosolvent is added to the $scCO_2$, the resulting intermediate polarity of the mixture can be tuned to match that of the desired compound.

Surfactants are the third type of additive mentioned above. These are compounds consisting of a $CO_2$-phobic head and $CO_2$-philic tail. The $CO_2$-phobic head could be either a hydrophilic polymer block or another polar functional group (ionized or not). The $CO_2$-philic tail is usually a long lipophilic polymer chain. This particular molecular structure provides the surfactants with the affinity to both polar and nonpolar phases. If a polar phase is present in the $CO_2$, surfactant molecules spontaneously adsorb on the interface building a "bridge" between both phases.

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[†] Part of the "Gerhard M. Schneider Festschrift".

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10.1021/je800875k CCC: $40.75

Here, we address the decontamination of very specific VLANW. These are polymeric matrixes contaminated with surface adherent plutonium dioxide ($PuO_2$) powder. It must be underlined that the contaminant is deposited on the surface of the polymer substrate in the absence of any covalent chemical bonding. Classical decontamination techniques such as solubilization of the $PuO_2$ in aqueous media imply the use of very aggressive acidic mixtures[20] and generate a large amount of secondary effluents which cause issues in terms of management. To reduce the secondary effluents to a minimum, our approach is to remove and to concentrate the $PuO_2$ particles using surfactants to enhance its dispersion in compressed $CO_2$. In this scenario, the $CO_2$ is used as a fluid in which the contaminant will be dispersed. The surfactant role is, on one hand, to enhance the $PuO_2/CO_2$ interactions and, on the other hand, to reduce the attractive van der Waals forces between the $PuO_2$ particles and the solid substrate. This decontamination process has been patented in 2007.[21]

Obviously, the decontamination efficiency will be closely related to the surfactant solubility and interfacial activity. The surfactant should exhibit the lowest possible cloud-point pressure (i.e., highly soluble in the $CO_2$ medium) to operate at mild conditions of temperature and pressure. In addition, the surfactant interfacial activity should be high enough to overcome the attractive van der Waals forces between the $PuO_2$ and the substrate.

In this study, the attention is focused on a special class of trade hydrocarbonated surfactants known as "Pluronics". These are linear amphiphilic triblock copolymers of poly(ethylene oxide) (PEO or $(EO)_x$ where $x$ is the number average degree of polymerization of ethylene oxide) and poly(propylene oxide) (PPO or $(PO)_y$ where $y$ is the number average degree of polymerization of propylene oxide).

There exist two different types of Pluronic copolymers: the Pluronic L and R series. The L series are copolymers where the structure consists of a central PPO block and two outer PEO blocks: $(EO)_x-(PO)_y-(EO)_x$. The R series are also triblock copolymers but with a different block sequence. In this case, a central PEO block is connected to two terminal PPO blocks: $(PO)_y-(EO)_x-(PO)_y$. It should be underlined that in the two series each terminal block is hydroxyl (OH) terminated. The L series has two terminal primary OH groups, while the R series has two secondary OH groups.

The $(PO)_y$ block(s) act(s) as the $CO_2$-philic part(s) of the surfactant, while the $(EO)_x$ block(s) act(s) as the $CO_2$-phobic one(s). As a result, by changing the $x$ and $y$ values, the hydrophilic/$CO_2$-philic balance (HCB) accounting for the surfactant interfacial activity can easily be tuned. Varying $x$ and $y$, however, also leads to changes in the phase behavior of the surfactant in $CO_2$.

The existing Pluronics classification system is based on the copolymer type (L or R), the total number average molar mass ($M$), and the amount of PEO within the copolymer structure (the PEO/$M$ ratio, i.e., the mass fraction of PEO within the copolymer). Unfortunately, knowing only these parameters, it is not directly possible to predict the surfactant phase behavior although an empirical approach has been proposed.[17] Moreover, because of the large variety of the Pluronics family, to check each Pluronic's phase behavior experimentally is very time-consuming. Therefore, a more theoretical approach for surfactant characterization and selection is required.

For this purpose, the perturbed-chain statistical association fluid theory (PC-SAFT) model is applied to predict and to correlate the Pluronics' phase behavior depending on their structure, $M$ and PEO/$M$ ratio. The goal is to use the PC-SAFT model as a tool for surfactant selection regarding the decontamination of surface-adherent $PuO_2$ particles.

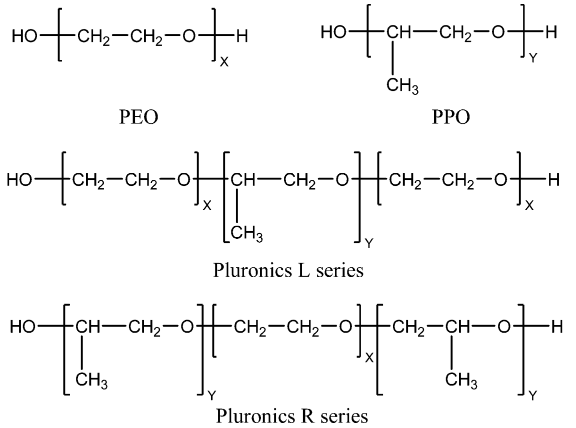

**Figure 1.** Chemical structures of PEO, PPO, Pluronics L, and Pluronics R polymers.

## PC-SAFT Model

Only a very general description of the PC-SAFT model related to the modeling of the Pluronics + $CO_2$ system is presented here. A more detailed description regarding the model development can be found in Gross and Sadowski.[22,23]

Within the PC-SAFT framework, molecules (regular compounds and homopolymers) are assumed to be chains of equal-sized spherical segments interacting according to a repulsive/attractive potential. To describe copolymers, the model is allowed to account for different types of segments within a single polymer chain.[24–26] If we take the Pluronics as an example, one type of segment is assigned to the PEO part of the molecule and another type to the PPO part.

In terms of the residual Helmholtz energy ($a^{\mathrm{res}}$), the general expression of the PC-SAFT model is given as a sum of three contributions: hard-chain ($a^{\mathrm{hc}}$), dispersion ($a^{\mathrm{disp}}$), and association ($a^{\mathrm{assoc}}$), respectively

$$a^{\mathrm{res}} = a^{\mathrm{hc}} + a^{\mathrm{disp}} + a^{\mathrm{assoc}} \tag{1}$$

A nonassociating molecule is described by three pure-component parameters. These are, namely, the segment number $m$, the temperature-independent segment diameter $\sigma$, and the dispersion energy between two segments $\varepsilon/k$.

To account for different segment types $\alpha$ and $\beta$ in a molecule, one-fluid mixing rules are applied as

$$\varepsilon_{\alpha\beta}/k = \sqrt{\varepsilon_\alpha/k \cdot \varepsilon_\beta/k} \cdot (1 - k_{\alpha\beta}) \tag{2}$$

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta) \tag{3}$$

The binary interaction parameter $k_{\alpha\beta}$ corrects the cross-dispersive energy between segments $\alpha$ and $\beta$.

The PEO, PPO, and Pluronic copolymers have two terminal OH groups (see Figure 1) which are able to form hydrogen bonds. To describe the association, one proton donor (A) and one proton acceptor (B) interaction site is assumed for each hydroxyl group (Figure 2). In addition, the association energy of both oxygen−oxygen and hydrogen−hydrogen (AA and BB)

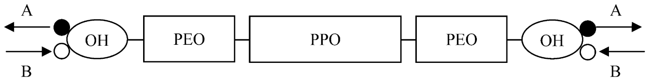

**Figure 2.** Schematic presentation of a Pluronic L molecule indicating the proton donor (A) and proton acceptor (B) interaction sites.

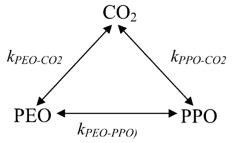

**Figure 3.** Schematic presentation of the three binary interaction parameters as characteristic of each interacting segment couple.

**Table 1. Structures and Physicochemical Properties of Studied Pluronics**

| polymer | structure[a] | $M$/(g·mol$^{-1}$)[b] | (PEO/$M$)/%[b] |
|---|---|---|---|
| PPO2000 | $(PO)_{34}$ | 2000 | 0 |
| PPO4000 | $(PO)_{69}$ | 4000 | 0 |
| L61 | $(EO)_2-(PO)_{31}-(EO)_2$ | 2000 | 10 |
| L81 | $(EO)_3-(PO)_{42}-(EO)_3$ | 2750 | 10 |
| L62 | $(EO)_5-(PO)_{34}-(EO)_5$ | 2500 | 20 |
| 17R2 | $(PO)_{15}-(EO)_{10}-(PO)_{15}$ | 2150 | 20 |
| 17R4 | $(PO)_{15}-(EO)_{26}-(PO)_{15}$ | 2700 | 40 |
| 25R2 | $(PO)_{22}-(EO)_{14}-(PO)_{22}$ | 3100 | 20 |

[a] $x$ and $y$ values calculated using the molar mass $M$ and the PEO mass fraction PEO/$M$ of the polymers. [b] Molar mass $M$ and PEO mass fraction PEO/$M$ values obtained from BASF and M. Ash.[31]

interactions is assumed to be equal to zero. Therefore, the only nonzero association energy is due to the unlike oxygen−hydrogen and hydrogen−oxygen (AB and BA) interactions which moreover are considered as equivalent.[27] Moreover, intramolecular H bonding is not explicitly considered, and thus the OH groups can associate only with those of other copolymer chains or with solvent molecules. Using Rayleigh Wing and FTIR spectroscopy, Crupi et al.[28] confirm this assumption. They have concluded that for steric hindrance reasons the intramolecular hydrogen bounding in liquid PEO with molar masses ranging from (200 to 2000) g·mol$^{-1}$ is of very low probability.

To account for the self-association, two additional pure-component parameters are required. The first one is the association energy between sites A and B of chains $i$ and $j$, $\varepsilon^{A_iB_j}/k$. The second associating parameter is a dimensionless parameter accounting for the associating volume, $\kappa^{A_iB_j}$.

Usually the pure-component parameters are determined by fitting to vapor pressures and liquid-density data. This method is well-defined for volatile compounds with low molar mass. Unfortunately, since no vapor pressure data are accessible for high molar mass polymers, the pure-component parameters of the polymers adjusted only to liquid density data give inappropriate values. In this case, the values of $\sigma$ and $\varepsilon/k$ are often overestimated, and the values of $m$ tend to be underestimated thus leading to unsatisfactory results[29,30] for the mixture.

Alternatively, the pure-component and the respective binary interaction parameters can be determined by simultaneously fitting to liquid-density data and to binary equilibrium data of one homopolymer + solvent system. It has been shown that usually the pure-component parameters obtained this way are suitable also for other solvent systems and can thus be regarded as being characteristic of the homopolymer.[22]

Additionally, three binary interaction parameters are required. As can be seen in Figure 3, two of these parameters account for the interactions between each type of segment and $CO_2$ ($k_{\text{PEO-CO2}}$ and $k_{\text{PPO-CO2}}$). They are determined independently of the copolymer data from binary equilibrium data of the respective homopolymer + solvent mixtures. The third parameter ($k_{\text{PEO-PPO}}$) accounts for the interactions between the PEO and PPO segments of different copolymer chains according to eq 2. This is the only parameter that needs to be determined from binary copolymer + $CO_2$ data.

## Experimental Section

***Materials.*** $CO_2$ (99.99992 % purity) was purchased from Linde Gas (France). PPO homopolymers with molar masses of (2000 and 4000) g·mol$^{-1}$ were purchased from Aldrich (99.8 % purity). Three $(EO)_x-(PO)_y-(EO)_x$ copolymers referred to as Pluronics L61, L62, and L81 were provided by BASF SE (Germany). They were used as received without further purification. L61 and L81 exhibit an amount of PEO in the copolymer molecule of about 10 wt %, whereas the L62 has a PEO amount of about 20 wt %. Figure 1 and Table 1 give additional structural information. The data regarding the molar mass of the copolymers are taken from BASF SE and from M. Ash.[31] The polydispersity index (PDI) of the samples was determined by size exclusion chromatography (SEC). SEC was performed using a Spectra Physics Instruments SP8810 pump equipped with a Shodex RIse-61 refractometer detector and two 300 mm columns mixed-C PL-gel 5 μm (molar mass range from ($2 \cdot 10^2$ to $2 \cdot 10^6$) g·mol$^{-1}$) from Polymer Laboratories (at $T$ = 303 K). Tetrahydrofuran was used as eluent at a flow rate of 1.0 cm$^3$·min$^{-1}$. Calibration was performed with polystyrene standards from Polymer Laboratories. Mark−Houwink coefficients were applied with the following values: polystyrene ($K = 11.4 \cdot 10^{-3}$ cm$^3$·g$^{-1}$, $\alpha = 0.716$)[32] and poly(propylene oxide) ($K = 55 \cdot 10^{-3}$ cm$^3$·g$^{-1}$, $\alpha = 0.620$).[33] SEC results have shown that PDI indexes of all studied polymers are in the limits from 1.02 to 1.09. Therefore, the polydispersity will not be explicitly considered for the modeling.

***Cloud-Point Measurements.*** Cloud-point measurements were carried out in a high-pressure variable-volume view cell ($P_{\max}$ = 40 MPa) having a maximum volume of 15 cm$^3$ (Top Industrie, France). The cell was equipped with a sapphire window for visual observations. The pressure was varied at constant system composition using a moving piston inside the cell. The pressure was measured using a pressure transducer from Top Industrie (504 series, 100 MPa, uncertainty ± 0.25 %) equipped with a pressure numerical display from Top Industrie (uncertainty ± 0.03 %). The temperature was measured using an internal type K thermocouple (Thermocoax TKA15/10) equipped with a temperature numerical display from Top Industrie (uncertainty of ± 0.5 at 298.13 K).

The cell was equipped with a rupture disk and an internal thermocouple and was thermostatted by a water + isopropanol mixture delivered by a circulating pump (RE 206, LAUDA, USA). The $CO_2$ was injected into the cell by an automatic syringe pump (260D, ISCO, USA). The concentration (in mass fraction $w$) was determined by knowing the mass of the sample and the mass of the $CO_2$ delivered into the cell by the syringe pump (volume change of the pump multiplied by the density of the $CO_2$ at given temperature and pressure). The uncertainty in mass fraction determination is estimated to be ± 4 %. Cloud-point measurements were performed by decreasing the pressure from about 35 MPa until the surfactant begins to precipitate out of solution; i.e., cloud point was defined as the reversible onset of a fully opaque solution. The determination of the cloud-point pressure was conducted thrice for each temperature. The measurement uncertainty is in the limits of ± 0.5 MPa depending on the polydispersity of the sample. For more details about the experimental procedure, the reader is referred to the

**Table 2. Experimental Cloud-Point Data for Studied Polymers at Given Mass Fraction of Polymer $w_{\text{Polymer}}$/% in $CO_2$[a]**

| polymer | $w_{\text{Polymer}}$/% | $T$/K | $p$/MPa | $T$/K | $p$/MPa |
|---|---|---|---|---|---|
| PPO2000 | 0.07 | 298.8 | 12.4 | 323.7 | 20.1 |
| | | 303.2 | 14.1 | 328.3 | 20.9 |
| | | 308.5 | 15.7 | 333.0 | 21.9 |
| | | 313.3 | 17.4 | 336.3 | 22.6 |
| | | 318.6 | 18.8 | | |
| PPO4000 | 0.05 | 312.9 | 29.3 | 323.8 | 32.2 |
| | | 313.3 | 29.4 | 328.0 | 33.2 |
| | | 317.6 | 30.5 | 328.5 | 33.3 |
| | | 318.1 | 30.8 | 332.8 | 34.4 |
| | | 322.3 | 31.7 | | |
| L61 | 0.08 | 293.1 | 11.5 | 318.2 | 19.8 |
| | | 299.2 | 13.7 | 322.3 | 21.1 |
| | | 303.7 | 15.5 | 328.2 | 22.4 |
| | | 308.4 | 16.9 | 332.5 | 23.9 |
| | | 313.1 | 18.4 | 337.3 | 25.1 |
| L81 | 0.08 | 294.1 | 18.4 | 318.1 | 24.4 |
| | | 298.9 | 19.6 | 323.6 | 25.8 |
| | | 303.3 | 20.7 | 328.2 | 26.9 |
| | | 308.1 | 22.2 | 332.8 | 28.2 |
| | | 312.5 | 23.2 | 337.1 | 29.0 |
| L62 | 0.1 | 293.4 | 22.7 | 319.2 | 27.7 |
| | | 298.6 | 23.4 | 323.3 | 28.6 |
| | | 303.4 | 24.6 | 328.6 | 29.3 |
| | | 308.3 | 25.6 | 335.5 | 31.3 |
| | | 313.1 | 26.6 | | |

[a] The cloud-point determination uncertainty is ± 0.5 MPa.

**Table 3. Pure-Component and Binary Interaction Parameters Used for the Modeling of the Homopolymer Cloud-Point Data**

| | pure-component parameters | | | | | |
|---|---|---|---|---|---|---|
| component | $(m/M)$ mol·g$^{-1}$[a] | $\sigma$ Å | $(\varepsilon/k)$ K | $(\varepsilon^{A_iB_j}/k)$ K | $\kappa^{A_iB_j}$ | ref |
| PEO | $5.06\cdot10^{-2}$ | 2.8999 | 204.60 | 1799.80 | $2.00\cdot10^{-2}$ | this study |
| PPO | $3.63\cdot10^{-2}$ | 3.3500 | 190.49 | 1749.0 | $2.98\cdot10^{-2}$ | this study |
| $CO_2$ | $4.71\cdot10^{-2}$ | 2.7851 | 169.2 | – | – | ref 23 |
| | Binary Interaction Parameters | | | | | |
| | $k_{\text{PEO-CO2}} = 0.013$ | | | | | this study |
| | $k_{\text{PPO-CO2}} = 0.056$ | | | | | this study |

[a] The segment number $m$ is given as $m/M$ where $M$ is the molar mass of the $CO_2$ or the homopolymer repeat unit.

previous study of Galy et al.[17] Table 2 summarizes the experimental cloud-point data obtained for all studied polymers.

## Results and Discussion

***Parameter Estimation.*** As discussed previously, the five pure-component parameters of the homopolymers as well as the respective homopolymer + $CO_2$ binary interaction parameters are adjusted simultaneously to homopolymer liquid-density data and to binary homopolymer + $CO_2$ (cloud-point) data. The polydispersity of the two homopolymers was not explicitly considered for the parameter determination. The required $CO_2$ parameters were taken from the literature (Table 3).[23,34]

The parameter set for PEO was determined for a homopolymer (Figure 1) with molar mass of 600 g·mol$^{-1}$ (PEO600). Liquid-density data for PEO600 was taken from Zoller and Walsh.[35] For cloud-point data in carbon dioxide, we took advantage of the experimental data published by O'Neill et al.[36] for PEO600 at $w$ = (0.296, 0.610, and 0.924) %, respectively. The PEO600s pure-component and the respective binary interaction parameters with carbon dioxide were first adjusted to the cloud-point pressure curve at a polymer mass fraction of 0.296 % shown in Figure 4. Using these parameters (Table 3), the cloud-point curves at the polymer mass fractions of $w$ = 0.610 % and $w$ = 0.924 % were predicted. The resulting binary equilibrium curves accurately describe the concentration dependence of the cloud-point pressure as can be seen from Figure 4.

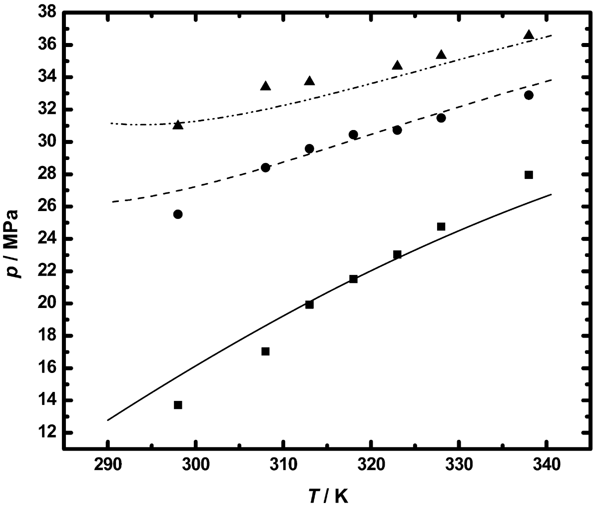

**Figure 4.** Cloud-point pressures of PEO ($M$ = 600 g·mol$^{-1}$) in carbon dioxide as a function of temperature. Symbols are experimental data obtained from O'Neill et al.[36] for: ■, $w$ = 0.296 %; ●, $w$ = 0.610 %; and ▲, $w$ = 0.924 %. Lines are PC-SAFT calculations: —, is a fit to $w$ = 0.296 % using $k_{\text{PEO-CO2}}$ = 0.013; --- and -·· are predictions for $w$ = 0.610 % and $w$ = 0.924 %, respectively, using the same $k_{\text{PEO-CO2}}$ = 0.013.

The PPO parameter set was determined for homopolymers (Figure 1) with molar masses of 2000 (PPO2000) and 4000 g·mol$^{-1}$ (PPO4000). Liquid-density data were again taken from Zoller and Walsh.[35] For the needs of this study, binary equilibrium of the two PPO homopolymers in carbon dioxide was measured at $w$ = 0.07 % (PPO2000) and $w$ = 0.05 % (PPO4000) (see Table 2).

The same modeling strategy was applied to the PPO + $CO_2$ systems. The five pure-component parameters of the homopolymer have first been fitted to the lower molar mass cloud-point curve (PPO2000 at $w$ = 0.07 %). The value of the binary interaction parameter $k_{\text{PPO-CO2}}$ has been determined to be equal to 0.056. Using these parameters (Table 3), a pure prediction was done for the higher molar mass homopolymer PPO4000 at $w$ = 0.05 % in carbon dioxide. As can be seen in Figure 5, the model again accurately describes the molar mass dependence of the cloud-point pressure. The prediction for PPO4000 is less accurate than for the PEO system but remains within acceptable limits.

The higher solubility of PPO versus PEO in compressed $CO_2$ at a given molar mass can be explained by the weaker segment–segment interactions for PPO due to steric hindrance. This assumption is confirmed by the lower value of the segment–segment attraction energy ($\varepsilon/k$) of the PPO. In addition to that, the higher solubility of PPO can also be ascribed to the lower polarity of the secondary OH groups, thus leading to weaker self-association by hydrogen bonding. This conclusion is consistent with the stronger acidity for primary alcohols (ethanol, p$K_a$ = 16) relative to secondary alcohols (isopropanol, p$K_a$ = 17.1).[37]

***Modeling Copolymer Pluronics L + $CO_2$ Binary Equilibrium Data. Pluronics L61 and L81.*** As presented in Figure 1, Pluronics L are linear triblock copolymers with a central PPO block connected from both sides to two PEO blocks. Each PEO block has one terminal OH group. As discussed in the previous section, the set of pure-component and respective homopolymer

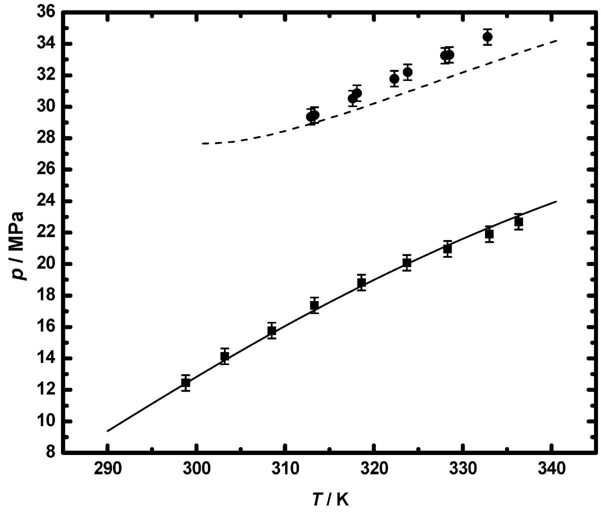

**Figure 5.** Cloud-point pressures of PPO ($M$ = (2000 and 4000) g·mol$^{-1}$) in carbon dioxide as a function of temperature. Symbols are experimental data obtained in this study for: ■, $w = 0.07$ % PPO 2000 g·mol$^{-1}$; and ●, $w = 0.05$ % PPO 4000 g·mol$^{-1}$. Lines are PC-SAFT calculations: —, a fit to $w = 0.07$ % PPO 2000 g·mol$^{-1}$ using $k_{\text{PPO-CO2}} = 0.056$; ---, a prediction for $w = 0.05$ % PPO 4000 g·mol$^{-1}$ using the same $k_{\text{PPO-CO2}} = 0.056$.

+ $CO_2$ binary interaction parameters was fitted to OH-terminated homopolymers. Considering that in the Pluronics structure the two terminal OH groups of the PPO block are substituted with two PEO blocks, we consider this central block to be nonassociative. Thus, for the modeling of the Pluronics L + $CO_2$ system, the two pure-component association parameters ($\varepsilon^{A_iB_j}/k$ and $\kappa^{A_iB_j}$) for PPO were not taken into account.

The two Pluronic copolymers considered in this section have a constant PEO/$M$ ratio of about 10 %. The attention here will be focused on defining the value of the binary interaction parameter $k_{\text{PEO-PPO}}$ that accounts for the interactions between PEO and PPO segments in the copolymer system. For that purpose, copolymer cloud-point pressures were measured at $w = 0.08$ % (L61 and L81) in carbon dioxide (see Table 2).

The applied modeling strategy was first to describe the phase behavior of the copolymer with the lower molar mass and the lowest cloud-point pressure (L61) by optimizing the $k_{\text{PEO-PPO}}$ parameter. For L61 already the pure model prediction using $k_{\text{PEO-PPO}} = 0$ is in good agreement with the experimental data (Figure 6). This confirms that the pure-component and the two homopolymer + $CO_2$ binary interaction parameters are very well defined. However, to improve the simulation quality, the value of the $k_{\text{PEO-PPO}}$ was slightly adjusted to 0.007 which results in an almost perfect fit with the experimental data for L61. This $k_{\text{PEO-PPO}}$ was then used to predict the cloud points of L81. Again, a very good agreement between the PC-SAFT prediction and the experimental data has been observed for L81.

Further studies on the mass fraction dependence have been performed to confirm the so-defined model parameters. To this aim, we took advantage of the binary equilibrium data for L61 ($w = 0.27$ %) and L81 ($w = 0.12$ %) in carbon dioxide published by O'Neill et al.[36] As can be seen in Figure 7, the model predictions using $k_{\text{PEO-PPO}} = 0.007$ agree with these experimental data within acceptable limits. The deviation can be explained with the fact that the current PC-SAFT calculations do not explicitly account for the polydispersity of the samples. In addition to that, O'Neill et al.[36] report uncertainties of their cloud-point measurement of up to 2 MPa for high polydispersities.

Thus, we can conclude that the model accurately describes and even predicts the increase in cloud-point pressure with an increase of the total molar mass for Pluronics L at a constant PEO/$M$ ratio. The model also accurately describes the concentration dependence for L61 and L81.

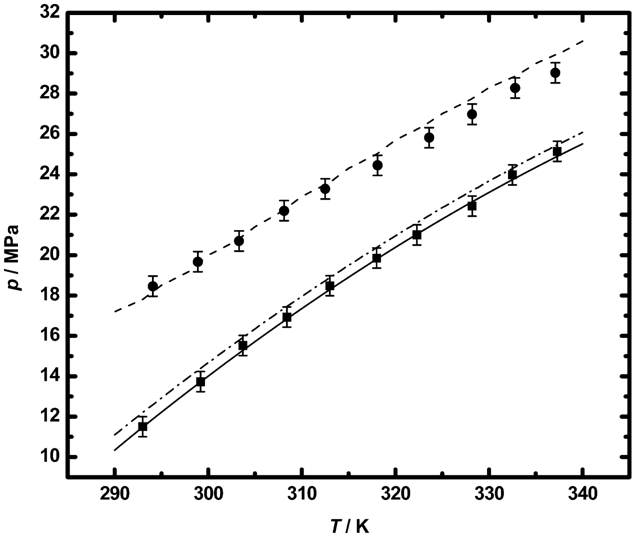

**Figure 6.** Cloud-point pressures of L61 and L81 in carbon dioxide as a function of temperature. Symbols are experimental data obtained in this study for: ■, $w = 0.08$ % L61; and ●, $w = 0.08$ % L81. Lines are PC-SAFT calculations: -•-, a pure prediction for L61 using only the pure-component parameters ($k_{\text{PEO-PPO}} = 0$); —, fit for L61 using $k_{\text{PEO-PPO}} = 0.007$; ---, prediction for L81 using $k_{\text{PEO-PPO}} = 0.007$.

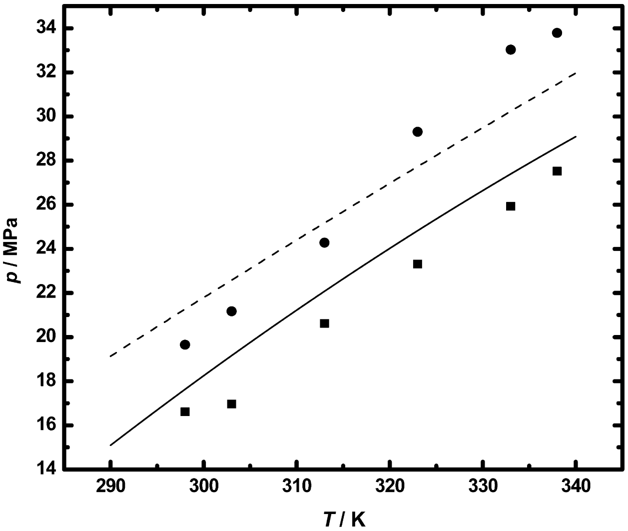

**Figure 7.** Cloud-point pressures of L61 and L81 in carbon dioxide as a function of temperature. Symbols are experimental data obtained from O'Neill et al.[36] for: ■, $w = 0.27$ % L61; and ●, $w = 0.12$ % L81. Lines are PC-SAFT predictions: —, $w = 0.27$ % L61; and ---, $w = 0.12$ % L81, respectively, using $k_{\text{PEO-PPO}} = 0.007$.

***Pluronic L62.*** In this section, the model flexibility to describe copolymers having higher PEO/$M$ ratios is investigated. The main goal here is to better understand the relationship between the PEO/$M$ ratio and the copolymer solubility.

For that purpose, the attention is focused on L62. This is a Pluronics L copolymer having a PEO/$M$ ratio of 20 %. The modeling was carried out using cloud-point data for $w = 0.1$ % available in Table 2 (this study) and for $w = 0.21$ % (O'Neill et al.[36]). The pure component as well as the binary interaction parameters are again taken from Table 3. Figure 8 summarizes the experimental data and the calculated PC-SAFT predictions for L62 at the two polymer concentrations.

The PC-SAFT prediction for L62 ($w = 0.1$ %) is in very good agreement with the experimental data. The prediction at

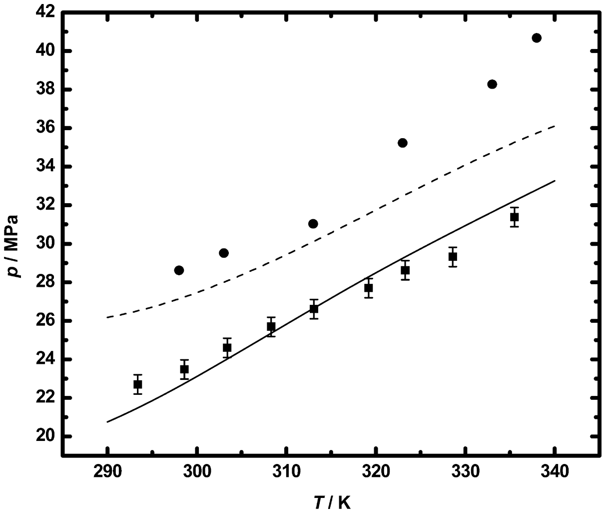

**Figure 8.** Cloud-point pressures of L62 in carbon dioxide as a function of temperature. Symbols are experimental data: ■, $w$ = 0.10 % L62 (this study); and ●, $w$ = 0.21 % L62 (O'Neill et al.[36]). Lines are PC-SAFT predictions: —, $w$ = 0.10 % of L62; and ---, $w$ = 0.21 % of L62 using $k_{\text{PEO-PPO}} = 0.007$.

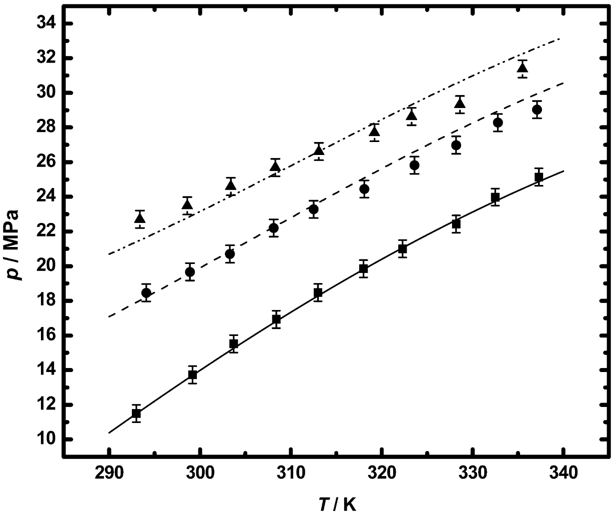

**Figure 9.** Cloud-point pressures of L61, L62, and L81 in carbon dioxide as function of temperature. Symbols are experimental data obtained in this study for: ■, $w$ = 0.08 % L61; ●, $w$ = 0.08 % L81; and ▲, $w$ = 0.1 % L62. Lines are PC-SAFT predictions calculated for: —, $w$ = 0.08 % L61; ---, $w$ = 0.08 % L81; and -••, $w$ = 0.1 % L62 using $k_{\text{PEO-PPO}} = 0.007$.

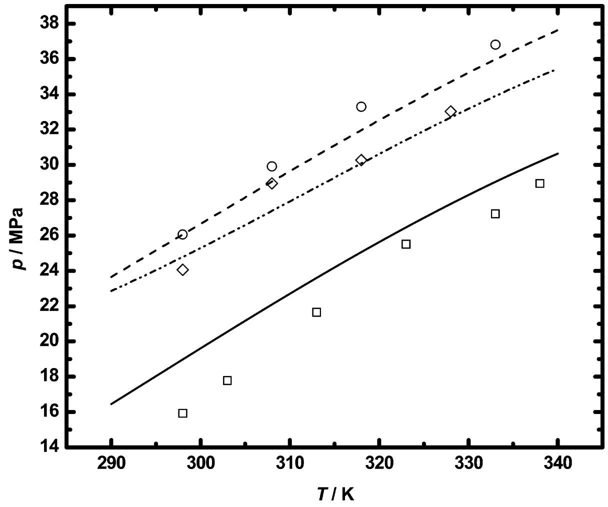

**Figure 10.** Cloud-point pressures of 17R2, 17R4, and 25R2 in carbon dioxide as a function of temperature. Symbols are experimental data obtained from O'Neill et al.[36] for: ○, $w$ = 0.13 % 17R4; ◇, $w$ = 0.13 % 25R2; and □, $w$ = 0.20 % 17R2. Lines are PC-SAFT calculations: ---, fit to $w$ = 0.13 % 17R4 using $k_{\text{PEO-PPO}} = -0.018$; — and -••, predictions for $w$ = 0.20 % 17R2 and $w$ = 0.13 % 25R2, respectively, using the same $k_{\text{PEO-PPO}} = -0.018$.

$w$ = 0.21 % is less accurate but still satisfactory. In this last case, the model predicts lower cloud-point pressures than the experimental data. The deviation increases with increasing temperatures from only 3 % at 298 K to more than 13 % at 338 K. As stated above, the deviation may be due to the difference in the sample polydispersities and in the experimental method used in this study and in that of O'Neill et al.

Figure 9 summarizes predictions for L61 ($w$ = 0.08 %) and L81 ($w$ = 0.08 %) compared to that of L62 ($w$ = 0.1 %). It can be easily seen from a comparison of L81 versus L62 that the experimental cloud-point pressure increases with the increase of the PEO/$M$ ratio at almost constant total molar mass and concentration. The respective PC-SAFT predictions follow the same tendency with very good accuracy. Comparing the structures of L61 ($M$ = 2000 g$\cdot$mol$^{-1}$, PEO/$M$ = 10 %) and L62 ($M$ = 2500 g$\cdot$mol$^{-1}$, PEO/$M$ = 20 %), it can be seen that both copolymers have a similar central PPO block: $M$ (PPO) = (1800 and 2000) g$\cdot$mol$^{-1}$, respectively. An increase in the experimental cloud-point pressure is observed when the molar mass of two terminal PEO blocks increases from (200 to 500) g$\cdot$mol$^{-1}$. This is expected since the $CO_2$-phobic character of the PEO block increases with its molar mass. This tendency is also accurately described by the model. The fact that no parameter changes are required for the modeling of Pluronics L copolymers with different $M$ and PEO/$M$ ratio suggests that, first, such copolymers behave the same way in the $CO_2$ medium and, second, that the self-association of the copolymer chains is independent of the $M$ and the PEO/$M$ ratio within the L series of copolymers.

***Modeling Pluronics R 17R2, 17R4, and 25R2.*** As a follow up of the very satisfactory results obtained for the Pluronics L copolymers, the model prediction capabilities were evaluated for the Pluronics R + $CO_2$ systems. It is important to note that the modeling was slightly modified since in contrast to the Pluronics L the Pluronics R have a central PEO block connected to two OH-terminated PPO blocks (see Figure 1). The modification consists in this time of turning off the association for PEO (setting the pure-component association parameters $\varepsilon^{A_iB_j/k}$ and $k^{A_iB_j}$ to zero) and allowing for those in PPO.

The modeling was carried out using cloud-point data for Pluronics R 17R2 ($w$ = 0.20 %), 17R4 ($w$ = 0.13 %), and 25R2 ($w$ = 0.13 %) published by O'Neill et al.[36] Additional structural information is given in Table 1.

The modeling of the Pluronics R phase behavior was first carried out using $k_{\text{PEO-PPO}}$= 0.007 as it was used in the case of the Pluronics L series. The resulting model predictions were in bad agreement with the experimental data. Therefore, a new value of the $k_{\text{PEO-PPO}} = -0.018$ was adjusted to the cloud-point curve of $w$ = 0.13 % 17R4. This $k_{\text{PEO-PPO}}$ was then used to predict the cloud points of 17R2 and 25R2. Figure 10 summarizes the experimental data of O'Neill et al.[36] and our respective model fit and predictions.

With the exception of 17R2, where the model predicts slightly higher cloud-point pressures, the PC-SAFT model describes accurately the experimental data.

The different value of $k_{\text{PEO-PPO}}$ can be explained by the slight modification of the model and/or by assuming that L and R type copolymers certainly behave differently. O'Neill et al. confirm this assumption by comparing the cloud-point curves of L62 ($w = 0.21$ %, Figure 8) and 17R2 ($w = 0.20$ %, Figure 10), which have the same PEO/*M* ratio and comparable molar masses: it can be easily seen that the L series is less soluble than the R one.

Two reasons can be pointed out to explain the higher solubility of the R type copolymers. The first one is related to the different $CO_2$-philic/$CO_2$-phobic balance between the PEO and the PPO blocks within the two copolymer types. A closer look at the molecular structures of the L62 ($(EO)_5-(PO)_{34}-(EO)_5$) and 17R2 ($(PO)_{15}-(EO)_{10}-(PO)_{15}$) shows that the molar mass per block of PEO increases from about 250 $g \cdot mol^{-1}$ (L62) to about 450 $g \cdot mol^{-1}$ (17R2). In contrast, the molar mass per block of PPO decreases from about 2000 $g \cdot mol^{-1}$ to about 900 $g \cdot mol^{-1}$, respectively. Knowing that the $CO_2$-phobic character of PEO and PPO increases with their molar mass, to explain the higher solubility of 17R2 one can draw the conclusion that the increase of $CO_2$-phobicity of the bigger PEO block is overwhelmed by the increased $CO_2$-philicity of the two smaller PPO blocks within the structure of 17R2.

As a second reason, one can point out the polarity difference of the terminal OH groups in both series. Weaker self-association due to hydrogen bounding is expected for Pluronics R copolymers because of the lower polarity and the higher steric hindrance of the secondary terminal OH groups.

Lastly, Pluronic copolymers might aggregate in $CO_2$ with complex micelle behavior. We have started small-angle neutron scattering studies on these systems to address this question, but the results are not conclusive yet. The formation of micellar aggregates of Pluronics in $CO_2$ might partly explain that the modeling approach requires two different $k_{PEO\text{-}PPO}$ values for related Pluronics L and Pluronics R, for instance. In this respect, micelles would have to be taken into account to improve the modeling of the data. This would undoubtedly be a challenge that would deserve attention in the future to overcome the limitations of the current model.

***Discussion Regarding Surfactant Selection.*** The selection of a surfactant for the decontamination process is based on two main criteria. First, for safety reasons, the working pressure of the decontamination process should be as low as possible. For instance, the maximal recommended operating pressure in this particular case is in the vicinity of 25 MPa. Since the surfactant is the key component of the process, the working pressure is closely related to its cloud-point pressure. Second, the interfacial activity of the surfactant should be sufficiently strong to overcome the attractive van der Waals forces between the contaminant and the solid substrate. It is important to point out that the role of the surfactant is not to completely eliminate the attractive forces but only to reduce them to levels where the plutonium dioxide particles can be more easily removed by the hydrodynamic flows due to the stirring of the system.

Both experimental data and model predictions have shown that surfactants with low molar mass and low PEO/*M* ratio are required to satisfy the first criterion. In addition, Pluronics R surfactants have been shown to exhibit higher solubility than the L series.

However, satisfying the first criterion does not automatically fulfill the second one. Often, surfactants with high solubility in $CO_2$ have low interfacial activity. Galy et al.[17,38] have confirmed this trend by studying the potential of L61, L81, and L101 to reduce the interfacial tension of a water + $CO_2$ system. They have shown that the interfacial activity of these surfactants increases in the order L61 < L81 < L101 while their $CO_2$-philic character, or their solubility, increases in the reverse order L101 < L81 < L61. Da Rocha et al.[19] have also shown that the efficiency of Pluronics to decrease the interfacial tension of the water + $CO_2$ system is closely related to the surfactant structure and PEO/*M* ratio. They have shown that Pluronics L copolymers lower the water + $CO_2$ interfacial tension more than the R ones. It appears that Pluronics L copolymers having a PEO/*M* ratio of 20 % are the most effective. As an example, the team of Da Rocha[19] has shown that the L62 is more efficient than all of the studied Pluronics R surfactants. The same activity trend should be observed in the present study since the $PuO_2$ is also a rather hydrophilic material.

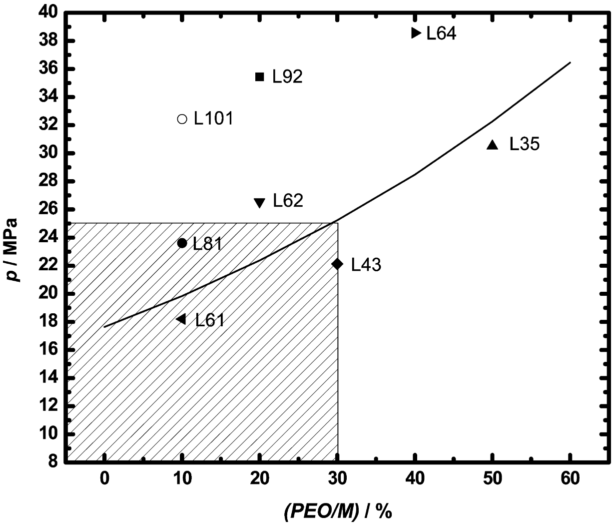

**Figure 11.** Calculated cloud-point pressure versus PEO mass fraction (PEO/*M*)/% for a number of Pluronics L copolymers. All calculations are made for a temperature of 313 K and a Pluronic mass fraction of $w = 0.1$ % in $CO_2$ using $k_{PEO\text{-}PPO} = 0.007$. Symbols are PC-SAFT predictions for: ■, L92 ($M = 3650$ $g \cdot mol^{-1}$); ▲, L35 ($M = 1900$ $g \cdot mol^{-1}$); ♦, L43 ($M = 1850$ $g \cdot mol^{-1}$); solid triangle pointing right, L64 ($M = 2900$ $g \cdot mol^{-1}$); solid triangle pointing left, L61 ($M = 2000$ $g \cdot mol^{-1}$); ▼, L62 ($M = 2500$ $g \cdot mol^{-1}$); ●, L81 ($M = 2750$ $g \cdot mol^{-1}$); ○, L101 ($M = 3800$ $g \cdot mol^{-1}$). The line (—) represents a PC-SAFT prediction for model Pluronic L copolymers with molar mass of 2000 $g \cdot mol^{-1}$ and different PEO/*M* mass fraction. The limits of 25 MPa and PEO/*M* mass fraction of 30 % define the region where compromise is possible.

Increasing the surfactant efficiency by increasing the PEO/*M* ratio is, unfortunately, in contradiction with the first criterion since the cloud-point pressure increases with the same ratio. Obviously, a certain compromise between efficiency and solubility should be considered.

Using the PC-SAFT model, it is possible to define the solubility regions at 313 K and $w = 0.1$ % of model L-type copolymers with a molar mass of 2000 $g \cdot mol^{-1}$ and a PEO/*M* ratio of up to 60 %. Figure 11 shows the calculated cloud-point pressures for various PEO/*M* ratios (solid line). The symbols represent the cloud-point pressures (predicted by the PC-SAFT model) of eight commercially available Pluronics L copolymers with different *M* and PEO/*M* ratios at the same temperature and concentration. The operation pressure limit of 25 MPa defines the domain where a compromise between efficiency and solubility is assumed to be acceptable.

It can be seen that to satisfy both criterions surfactants with low molar mass and a maximum of 30 % of the PEO/*M* ratio can be used. Predictions for $w = 0.1$ % of other Pluronics L surfactants are also shown in Figure 11. This shows that the part of the Pluronics family compatible with the decontamination process is actually quite limited. However, practical decontamination tests will show which surfactants perform well and which ones are the most effective for the removal of the surface adherent $PuO_2$ contaminant.

Importantly, the high cloud-point pressure of these surfactants makes the further optimization of the decontamination process, in terms of working pressure reduction, virtually impossible. Therefore, such optimization will require surfactants with lower solubility pressures. Polyfluorinated surfactants, for example, have been shown to exhibit a very high potential in particle removal and suspension stabilization in supercritical media.[18,39–42] However, despite their efficiency, such fluorinated compounds are also potential precursors of fluorine ($F_2$) and fluorohydric acid (HF) which must be avoided in the current waste management processes.

Knowing these limitations, in prospects, it will be interesting to study the possible applicability of another class of highly soluble surfactants: siloxylated surfactants. In majority, these are surfactants based on PDMS (poly(dimethyl siloxane)) which exhibit much lower solubility pressures at given concentration than the Pluronics. In addition, they also exhibit high interfacial activity and are commercially available in a large range of compositions.

## Conclusion

In this work, the PC-SAFT equation of state was used to model the phase behavior of L and R type Pluronics copolymers. It was also applied as a tool for surfactant selection regarding the removal of surface adherent $PuO_2$ particles from polymeric matrixes.

Pure-component parameters are fitted to hydroxyl terminated PEO and PPO homopolymers. In all studied systems, each OH group is considered as an associating site to form hydrogen bonds.

The PC-SAFT model is able to correlate the experimental data for L and R copolymers accurately. The model also accurately describes the increase in cloud-point pressure with increasing molar mass at constant PEO/$M$ ratio and with the PEO/$M$ at constant $M$.

Despite the huge variety of Pluronics copolymers and their low price, it has been shown that only a few of them could be used in a decontamination process. In particular, surfactants with a molar mass in the vicinity of 2500 $\mathrm{g \cdot mol^{-1}}$ and PEO/$M$ ratio lower or equal to 30 % should exhibit the highest decontamination efficiency.

Further optimization of the decontamination process will require surfactants soluble at lower pressures than the Pluronics. Therefore in perspectives, the attention will be focused on poly(dimethyl siloxane)-based surfactants.

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Received for review November 18, 2008. Accepted February 10, 2009. I. Stoychev acknowledges the Languedoc-Roussillon region for their financial support on this work (grant No.: 2006 Q-158). The authors also thank the German Science Foundation (DFG) for supporting this work with grant SA 700/14. The authors further thank the French Ministry of Foreign and European Affairs, CNRS, and CEA for their financial support on the French/German collaboration program - "P2R".

JE800875K