

Surfactant-Assisted Nuclear Decontamination Process of Solid Substrates in Supercritical CO₂: PC-SAFT Equation of State as a Tool for Modeling the Phase Behavior of Block and Graft PDMS-PEO Amphiphilic Copolymers

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ABSTRACT

The phase behavior of commercially available PDMS-g-PEO and PDMS-b-PEO surfactants (graft and block type poly(dimethyl siloxane)-poly(ethylene oxide) copolymers) was studied to evaluate their applicability in a supercritical CO₂ (scCO₂) based decontamination process. To this aim, experimental cloud points have been measured in scCO₂ using a classical variable-volume view-cell apparatus. The temperature and pressure ranges were from 298 to 338 K and from 5 to 40 MPa, respectively. The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) was used to model the experimental PDMS-PEO cloud-point curves. The phase behavior of the block copolymers could be described very accurately. A satisfactory description of the graft copolymers was achieved by accounting for the number of the grafted PEO branches. Applying PC-SAFT as a prediction tool, we managed to design an “optimized” surfactant for our needs – i.e. a surfactant with lowest-possible cloud-point pressures and a defined hydrophilic/CO₂-philic balance.

INTRODUCTION

In present days, the very-low-activity nuclear wastes (VLANW) present 90% of the total volume generated by the nuclear industry in the world. The VLANW include different type of solid substrates (e.g. gloves, tissues, soils, hardware etc...) which have been in contact with radioactive metals, oxides, or ions. Many decontamination techniques are applied in order to reduce the waste volume and to recover the radioactive elements. Unfortunately, these techniques are often economically unfavorable because of the large amount of contaminated organic solvents generated by the extraction processes.

Considering these limitations, scCO₂ is used instead of an organic solvent for the decontamination and the recovery of Plutonium dioxide (PuO₂) from specific type of VLANW. These VLANW represent used polymeric gloves contaminated by surface adherent PuO₂ powder. To overcome the polarity difference between the PuO₂ (polar contaminant) and the CO₂ (non-polar solvent) additives must be used. In recent years, polyfluorinated surfactants have shown to exhibit a very high potential in particle removal and suspension stabilization in supercritical media [1]. However, despite their efficiency, such fluorinated compounds are also precursors of fluorine (F₂) and fluorohydric acid (HF) which must be avoided in the current waste management processes. Therefore, we directed our research to study the possible applicability of the less expensive and more environmental-friendly PDMS—PEO surfactants. To predict and to assess the efficiency of a given PDMS—PEO

surfactant from the decontamination process's point of view, two criteria must be taken into account: (i) its cloud-point pressure should be as low as possible and (ii) its interfacial activity, which is a function of the PDMS/PEO ratio and the polymer structure, should be as strong as possible.

The main objective of the present work is to investigate the possibility to apply the PC-SAFT equation of state [2, 3] as a prediction tool for surfactant efficiency by taking into account the effect of the polymer composition and structure on its phase behavior (cloud point pressure). To this aim, cloud point pressures of two tri-block (PEO—PDMS—PEO) and four graft-type PDMS—PEO surfactants with molecular weights ranging from 600 to 3000 g/mol and a total amount of non-siloxane ranging from 40 to 70% have been investigated.

MATERIALS AND METHODS

Surfactants: Two different types of trade PDMS-PEO copolymer surfactants were purchased from Dow Corning®. The first type is a linear PEO-PDMS-PEO tri-block copolymer with molecular structure presented in **Figure 1-A**. The second type is a statistical graft-type copolymer with a PDMS backbone and a number of pendant PEO blocks – **Figure 1-B**.

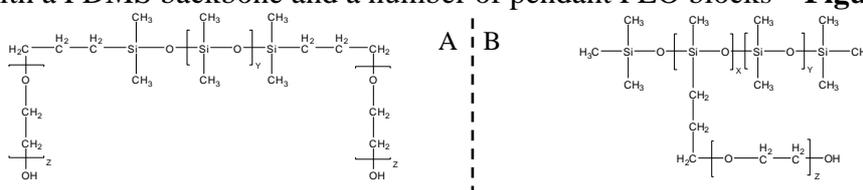


Figure 1: Copolymer structures: A – block type and B – graft type

In both copolymer types, each PEO block has a terminal “OH” group. Since these trade surfactants were products of industrial synthesis, no exact information about the polydispersity of the samples was available. The molecular weight (M_w) and the polymer composition were as follows: “193C Fluid” (graft, 3100 g/mol, 72%PEO), “Q2-5211 Superwetter” (graft, 600 g/mol, 68%PEO), “5103 Surfactant” (graft, 2500 g/mol, 65%PEO), “5097 Fluid” (graft, 2300 g/mol, 53%PEO), “Q4-3667 Fluid” (tri-block, 2200 g/mol, 55%PEO) and “2-8692 Fluid” (tri-block, 1900 g/mol, 41%PEO). All surfactants were used as received without any purification or other pre-treatment process.

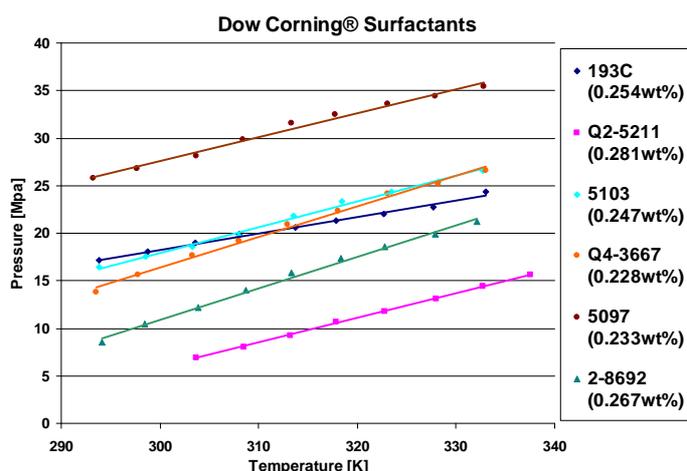


Figure 2: Surfactant's experimental cloud-point data. The solid lines are linear fits.

Cloud-point measurements: The data (**Figure 2**) were obtained by using a variable volume view cell as described elsewhere [4]. All measurements were made at relatively low copolymer concentrations of 0.2 – 0.3wt%. Each point on the cloud-point curves was obtained by slowly decreasing the system pressure at constant temperature. The temperature and pressure were maintained with an error of 0.1 K and 0.02 MPa, respectively. The cloud-point transition has occurred gradually

in pressure interval of 0.5 to 1.0 MPa which is consistent with the considerable polydispersity of the samples.

RESULTS AND DISCUSSION

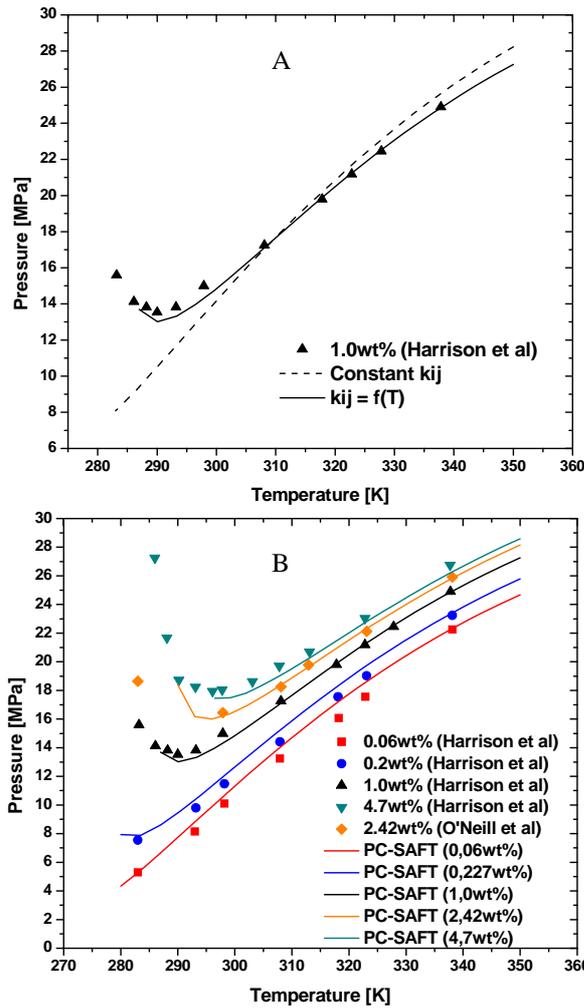


Figure 3: Modeling of cloud-point data for PDMS Homopolymer-CO₂ systems. A – Fitting $k_{ij}^{PDMS-CO_2}$ for 1wt% PDMS (13000 g/mol). B – Concentration dependency using $k_{ij}^{PDMS-CO_2} = f(T)$ for PDMS 13000 g/mol.

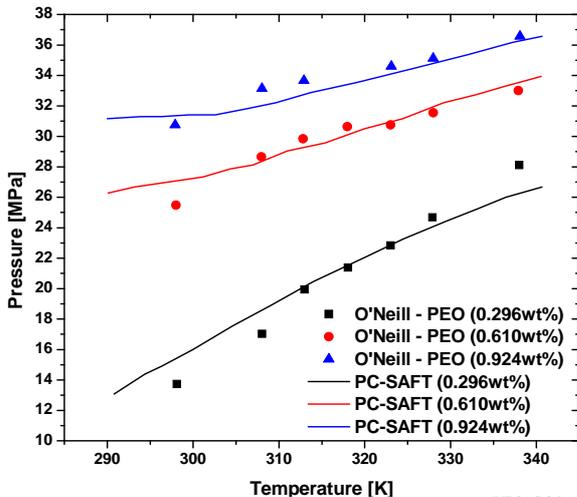


Figure 4: Concentration dependency using $k_{ij}^{PEO-CO_2} = 0.013$ for PEO 600 g/mol

Modeling homopolymer data:

The PC-SAFT modeling of the Dow Corning® surfactants requires the knowledge of the respective pure-component parameters of the homopolymers. The pure-component parameters (PCP) for PDMS were obtained earlier by Krüger et al. [5] for the PDMS/n-pentane system. These parameters were used here also for the PDMS/CO₂ system. A temperature-independent binary interaction parameter (BIP) $k_{ij}^{PDMS-CO_2}$ was adjusted to experimental cloud-point data from Harrison et al [6] and O'Neill et al [7] for 13000 g/mol PDMS homopolymer with low polydispersity. As it can be seen in **Figure 3-A** (dashed line), the model prediction using a constant value of $k_{ij}^{PDMS-CO_2} = 0.0465$ is in good agreement with the slope of the linear part of the curve.

However, to obtain improved results, a temperature-dependent binary interaction parameter was introduced. For this purpose, values for the $k_{ij}^{PDMS-CO_2}$ were first fitted for each point of the curve in Figure 3-A. The comparison of the PC-SAFT correlations using constant (dashed line) and temperature dependent BIP ($k_{ij}^{PDMS-CO_2} = 0.07565 - 9.40617E-5 * T$) (solid line) is also given in **Figure 3-A**. As it can be seen, the quite non-linear cloud-point behavior can be brought into excellent agreement to the experimental data using a linear temperature-dependent BIP.

Figure 3-B shows a concentration dependency analysis performed for PDMS 13000 g/mol using the same temperature dependent $k_{ij}^{PDMS-CO_2}$. As it can be seen, the cloud-point pressure curves at various copolymer concentrations can be very accurately predicted by the PC-SAFT model using the parameters obtained for the 1wt% PDMS. The bigger model discrepancies at higher concentrations and low temperatures do not concern our study since for decontamination processes, the surfactant concentration is generally less than 1wt%. The pure-component parameters for PEO were fitted in an earlier study by Galy [8] to PEO (600 g/mol) using PEO/CO₂ cloud-point data from O'Neill et al [7].

The respective $k_{ij}^{\text{PEO-CO}_2}$ is temperature independent and has a value of 0.013. The modeling results for different concentrations of PEO/CO₂ mixtures as depicted in **Figure 4** are in very good agreement to the experimental data.

The entire PCP sets for the CO₂ and the homopolymers as well as the respective BIP are presented in **Table 1**.

Component	m/M (mol.g ⁻¹)	σ (Å)	ϵ/k (K)	ϵ^{AiBj}/k (K)	κ^{AiBj}	Ref.
PDMS	$3.46 \cdot 10^{-2}$	3.382	165.0	-	-	[5]
PEO	$5.06 \cdot 10^{-2}$	2.8899	204.60	1799.80	$2 \cdot 10^{-2}$	[8]
CO ₂	$4.71 \cdot 10^{-2}$	2.7851	169.2	-	-	[9]
Binary Interaction parameters						
	$k_{ij}^{\text{PDMS-CO}_2}$	$0.07565 - 9.40617E-5 \cdot T$				
	$k_{ij}^{\text{PEO-CO}_2}$	0.013				
	$k_{ij}^{\text{PEO-PEO}}$ (block copolymers)	0.02				
	$k_{ij}^{\text{PEO-PEO}}$ (graft copolymers)	$0.5164 - 0.08699 \cdot (n^\circ \text{ "OH" groups})$				

Table 1: PCP and BIP values

Modeling copolymer phase behavior: The modeling of the block-copolymer phase behavior was carried out using the homopolymer's PCP (PDMS and PEO) as well as the BIP's $k_{ij}^{\text{PDMS-CO}_2}$ and $k_{ij}^{\text{PEO-CO}_2}$ as obtained for the binary homopolymer/CO₂ systems. The respective M_w and amount of PEO in the structure of both block copolymers were used for the modeling as obtained from the characterization procedure. The number of association sites was set to two - one proton donor and one proton acceptor association site - according to one "OH" group. The total number of "OH" groups was also set to two because each block copolymer had two terminal "OH" groups. The BIP $k_{ij}^{\text{PDMS-PEO}}$ was first fitted for the copolymer with the lowest M_w and %PEO ("2-8692 Fluid", 1900g/mol, 41%PEO). This $k_{ij}^{\text{PDMS-PEO}}$ was then used to predict the cloud-points of the "Q4-3667 Fluid" (2200 g/mol, 55%PEO).

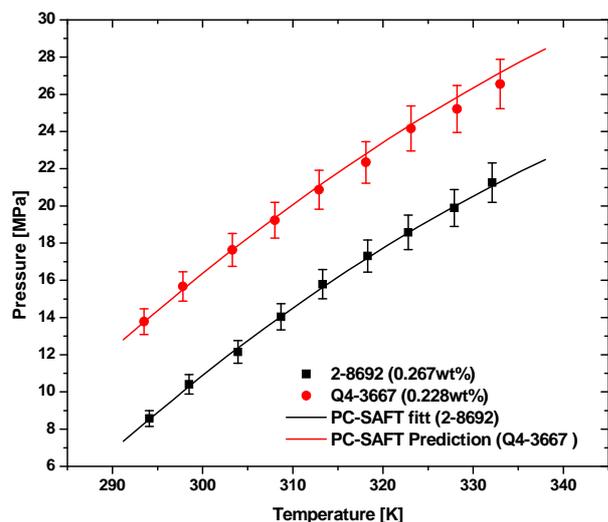


Figure 5: PC-SAFT calculated phase behaviour of block copolymers "2-8692 Fluid" and "Q4-3667 Fluid" using $k_{ij}^{\text{PDMS-PEO}} = 0.02$. The error bars define the range of $\pm 5\%$

The sample polydispersity was not explicitly considered, because no information where available for the investigated polymers. As it can be seen in **Figure 5**, the model predictions for both block copolymers using a constant BIP of $k_{ij}^{\text{PDMS-PEO}} = 0.02$ are in excellent agreement to the experimental within the experimental uncertainties of $\pm 5\%$.

In the case of block copolymers the molecular structure is well defined. The two degrees of freedom (molecular weight and amount of PEO in the copolymer) are directly accounted for in the PC-SAFT model. The description of the graft copolymers phase behavior is much more complex. These copolymers have two additional degrees of freedom which strongly

influence the phase behavior: the branch length and the branch distribution in the siloxane backbone

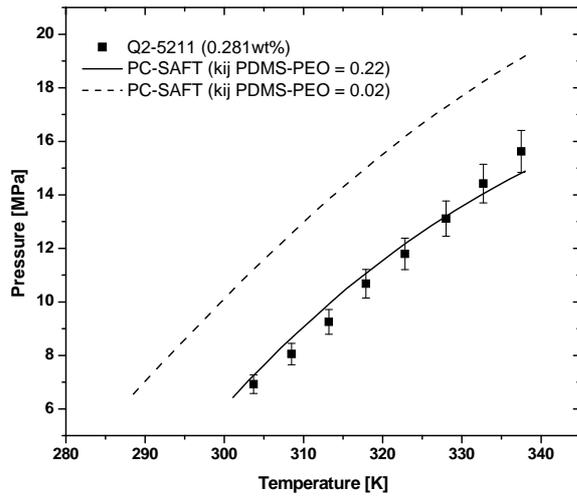


Figure 6: Modeling “Q2-5211 Superwetter” cloud point data using $k_{ij}^{\text{PDMS-PEO}} = 0.02$ (dashed line) and $k_{ij}^{\text{PDMS-PEO}} = 0.22$ (solid line). The error bars define the range of $\pm 5\%$

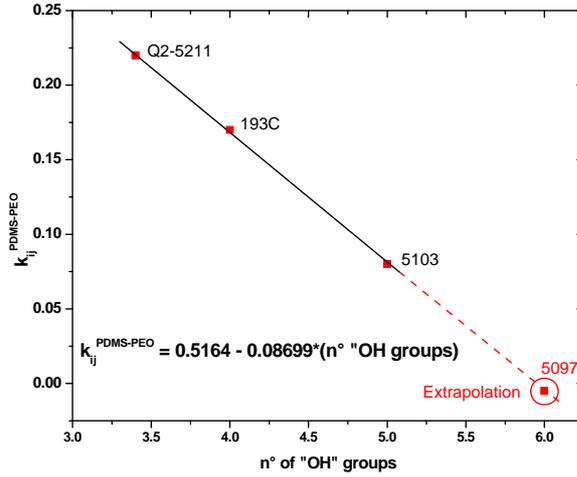


Figure 7: $k_{ij}^{\text{PDMS-PEO}}$ as a function of the number of “OH” groups

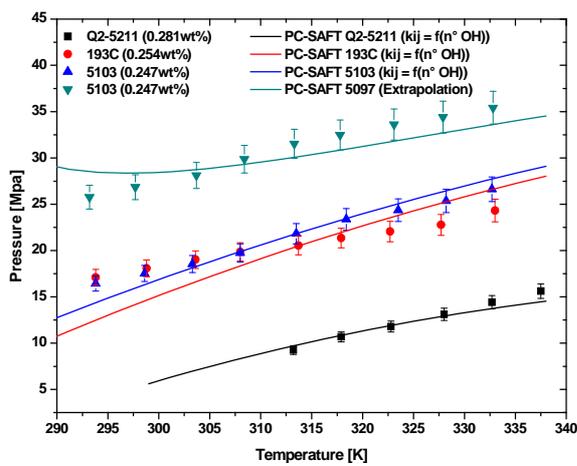


Figure 8: Experimental data and PC-SAFT predictions for all studied graft polymers. The error bars define the range of $\pm 5\%$

However, the classical PC-SAFT model can only explicitly consider type and number of associating sites and copolymer composition whereas the effect of branch length and branch distribution can not be directly accounted for. Since the OH groups are located each at the end of a branch, the “OH” number is assumed as equal of the specific branch number (estimated by Dow Corning) of each copolymer: “Q2-5211 Superwetter” – 3.4 “OH” groups, “193C Fluid” – 4 “OH” groups and “5103 Fluid” – 5 “OH” groups. Unfortunately, branch number data was not available for the “5097 Fluid”.

In a first step, predictions using $k_{ij}^{\text{PDMS-PEO}} = 0.02$ were carried out for the “Q2-5211 Superwetter”. However, as presented in **Figure 6** (dashed line), the predicted results do not capture the actual experimental data. Therefore, the $k_{ij}^{\text{PDMS-PEO}}$ was refitted for this particular graft copolymer. The new value was set to $k_{ij}^{\text{PDMS-PEO}} = 0.22$. Furthermore, the value of $k_{ij}^{\text{PDMS-PEO}}$ was refitted for “193C Fluid” (0.17) and “5103 Fluid” (0.08) too. Linear dependency was found when the graft $k_{ij}^{\text{PDMS-PEO}}$ parameter is plotted versus the “OH” number (**Figure 7**).

As previously discussed, no information about the grafted branches (“OH” groups) number is available for the “5097 Fluid”. However, in order to apply the proposed methodology for this surfactant, both the $k_{ij}^{\text{PDMS-PEO}}$ and “OH” number values for the “5097 Fluid” was extrapolated using the dependency presented in **Figure 7**. The model prediction for 5097 Fluid using the $k_{ij}^{\text{PDMS-PEO}}$ value calculated for six “OH” groups is in acceptable agreement with the experimental data (see **Figure 8**). The predictions made using seven and eight “OH” groups were situated at much higher pressures. In order to test this approach, further structural analysis is required to confirm or to reject the prediction made for “5097 Fluid” using six as branch number. The PC-SAFT predictions using the proposed modeling concepts show the following tendencies.

At constant amount of PEO in the copolymer, the cloud-point pressure rises with the number of grafted branches (the “OH” number). At the other hand, to maintain constant PEO amount, the branch length must decrease when their number increases. A cloud-point pressure decrease is expected when the length of the CO₂-phobic branches is lowered. But model predictions have shown that a graft copolymer (2000 g/mol, 60% PEO) with only one grafted branch is soluble at much lower pressures than an analog copolymer with six grafted branches. Therefore, it can be concluded that the positive effect of the reduced branch length on the cloud- point pressure is hidden by the negative one of the increased branch number.

Optimized surfactant. The PC-SAFT predictions have shown that block copolymers with M_w between 1000 and 3000 g/mol and with 40 to 50% of PEO have sufficiently low cloud-point pressures. We believe that this PDMS/PEO ratio is sufficient for good surfactant interfacial activity. In case of graft copolymers (1000 – 3000 g/mol, 40 – 50 % PEO) with 3 and 4 grafted branches, the predicted cloud-point pressures are in good agreement with our needs. Further interfacial activity tests are required to evaluate the efficiency of different PDMS-PEO surfactants with M_w and PDMS/PEO ration within these limits.

CONCLUSION

The phase behavior of the six Dow Corning® surfactants was successfully modeled using the PC-SAFT equation of state. We were able to draw the limits of M_w , PDMS/PEO ratio and polymer structure for surfactants optimized considering the limitations of the studied decontamination process.

ACKNOWLEDGMENT

I. Stoychev wishes to acknowledge the financial support Languedoc-Roussillon region on this work (grant No.: 2006 Q-158). The authors are also thankful to the German Science Foundation (DFC) for supporting this work with grant SA 700/14. The authors further wish to thank the French Ministry of Foreign and European Affairs for their financial support of the French/German collaboration program - “P2R”.

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