A study on melting point depression of fatty acids and Pluronics® in liquid or supercritical carbon dioxide

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Abstract

The melting behaviour of saturated fatty acids and Pluronics® was investigated in liquid or supercritical carbon dioxide ($SCCO_2$). Fatty acids included in this study were lauric acid, myristic acid, palmitic acid and stearic acid while Pluronics® used were F-77, F-127, F-68, F-38 and F-108. The melting point of fatty acids and Pluronics® was determined at pressure values from (7.0 to 50.0) MPa and (8.0 to 50) MPa respectively. Unprocessed and CO_2-processed samples of all fatty acids and Pluronics® were analysed by differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD). A melting point depression in the range of (18.1 to 19.3) °C was observed for the Pluronics® whereas the fatty acids showed a depression of (10.8 to 19.5) °C in their melting point. Interestingly, in case of fatty acids, the depression in melting point was found to be inversely proportional to the carbon chain length i.e. smaller the chain length, larger the depression. Therefore, as shown in the Table 1; Lauric acid which had the smallest carbon chain showed the highest depression of 19.5 °C.

Fatty Acid	**Melting point (°C)**	**Minimum melting point in CO_2 (°C)**	**Difference (°C)**
Lauric Acid	44.5	25.0 ± 0.2	19.5
Myristic Acid	54.4	41.2 ± 0.2	13.2
Palmitic Acid	63.0	51.1 ± 1.1	11.9
Stearic Acid	69.6	58.9 ±0.2	10.7

Table 1: Melting point depression of fatty acids

Another reason of this depression in melting point can be the solubility of CO_2 in fatty acids which in turn depends upon the extent of interaction between the CO_2 and functional groups present in the compound. Since CO_2 molecule has quadrupole moment, oxygen atom carries more electron density than carbon atom and this charge separation favours the interaction of CO_2 molecules with functional groups such as carboxylic acids, aldehydes and ketones.[1] The

effect of pressure was also studied on myristic, palmitic and stearic acid. It was found that initially the melting point decreases with increase in pressure and then increased after reaching a minimum. This can be explained by dominance of pressure effect over solubility effect at higher pressures.[2] Similarly, depression in melting point was also observed in all the studied Pluronics® but a different solid- liquid curve was observed. The solid-liquid curves for fatty acids and Pluronics® are shown in Figure 1 and 2.

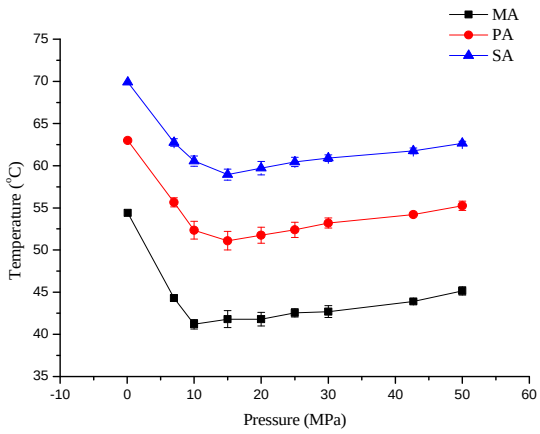

Figure 1: Solid-liquid curves for fatty acids

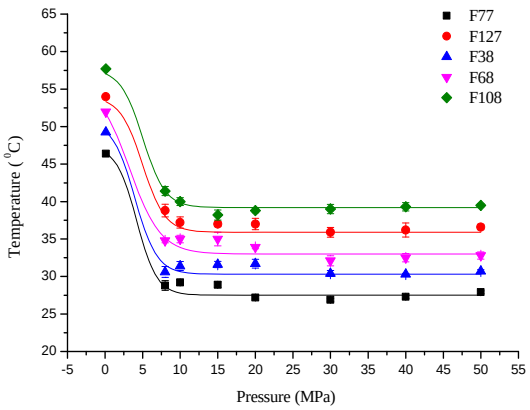

Figure 2: Solid-liquid curves for Pluronics®

The depression in melting point of Pluronics® can be due to the dissolution of CO_2 in the polymer matrix which increases the segment mobility and polymer free volume.[3] Interestingly, no effect of molecular weight and poly (ethylene) oxide content was found on melting point depression. Analysis by DSC and XRD revealed that CO_2 processing had no impact on the crystal morphology of Pluronics® and fatty acids.

This study provides a good understanding on the melting behaviour of fatty acids and Pluronics® in liquid or $SCCO_2$. Furthermore, this phenomenon can also be used in particle engineering at low temperatures and processing of thermolabile substances such as proteins and peptides.

References

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