

THE PHASE BEHAVIOR OF SYSTEMS OF SUPERCRITICAL CO₂ AND PROPANE WITH EDIBLE FATS

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The phase behavior of the systems CO₂ + rapeseed, CO₂ + tripalmitin and propane + rapeseed was studied experimentally according to the synthetic method using a so called Cailletet apparatus.

For the CO₂ + fat system bubble-point curves and solid-liquid curves were measured for fat concentrations from 70wt% up to 95wt%. At these concentrations the solidification temperature was below 67°C for both fats. For fat concentrations of 83 wt% and lower, the bubble point was above the critical pressure of carbon dioxide. A comparison was made between the phase behavior of these systems and the phase behavior of the systems propane + tripalmitin. It was found that supercritical CO₂ and propane dissolve well in different melts of edible fats. Compared to propane, higher pressures were needed for CO₂ in order to dissolve in the fat melt.

For the propane + fat system bubble-point curves, solid-liquid curves and liquid-liquid lower solution temperature curves were measured at fat concentrations from 30wt% up to 90wt%. At these concentrations the solidification temperature for the fat was below 61°C. It can be concluded that an increase in pressure or a decrease in temperature results in a higher solubility of carbon dioxide and propane in the fat melt. The measurements made it possible to predict qualitatively the phase behaviour of the CO₂ + fat and propane + fat systems. For CO₂ + fat systems a type III system with a metastable liquid-liquid phase split and for propane + fat systems a type IV phase diagram was observed according to the classification of van Konynenburg and Scott.

INTRODUCTION

Supercritical melt micronisation is considered to be an interesting technology to create near mono disperse particles of edible fats and waxes [1]. For this process CO₂ and propane appear to be suitable supercritical solvents. To develop this process reliable information on the phase behavior of CO₂ with edible fats or waxes and propane with edible fats or waxes is needed. Such information is not available in the open literature, except for data on the system propane + tripalmitin [3]. Therefore a study on the phase behavior of an edible fat mixture, rapeseed 70, and a pure edible fat, tripalmitin, with CO₂ and propane was performed.

MATERIALS AND METHODS

The CO₂ used was from Messer-Griessheim with a purity of 99.995% and the propane was also from Messer-Griessheim with a purity of 99.95%. Rapeseed 70 was obtained from Unilever/Vlaardingen and is mixture of different fatty acids. Tripalmitin was obtained from Sigma-Aldrich with a purity of 99%. All components were used without further purifications.

With a Cailletet apparatus phase transitions of mixtures of known composition can be determined visually including bubble-point curves, dew point curves and solid-solubility curves [2]. The mixture is first brought into a homogeneous state and the pressure or temperatures is varied until a second phase appears. The temperature is controlled within 0.02 K and measured with an accuracy of 0.01 K using PT-100 thermometer. The pressure is controlled and measured with a dead-weight gauge to within 0.05 bar. The errors in the weight fractions of the supercritical gas + fat mixtures are less than 0.1 wt%. The accuracy of the determination phase boundary pressures for the rapeseed 70 system was better than ± 0.2 bar and for the tripalmitin system better than ± 0.02 bar.

RESULTS AND DISCUSSION

In this section the liquid/vapour (L-V) and the solid-liquid (S-L) phase behavior of CO₂+ rapeseed 70, CO₂ + tripalmitin, propane + tripalmitin and propane + rapeseed system will be discussed.

In Figure 1, the phase behavior diagram of the CO₂ + rapeseed system is shown. The results from the solubility measurements are plotted in a *P-T* diagram as lines of constant composition (isopleths). The Figure shows bubble-point curves and solid-solubility curves. An increase in pressure or a decrease in temperature results in a higher solubility of carbon dioxide in the fat melts. By increasing the weight percentages of CO₂ in the rapeseed 70, higher pressures are needed to dissolve the CO₂ in the fat melt. The pressure ranges between 29 and 307 bar and the temperature between 325.15 K and 367.15 K. Solid-liquid equilibria were measured only for 83wt%, 90wt%, 95wt% and 100wt% of fat. As can be seen in Figure 1, the vertical S+L? L (liquidus) phase boundary curves shifts to lower temperatures with increasing CO₂ concentration indicating a melting point depression.

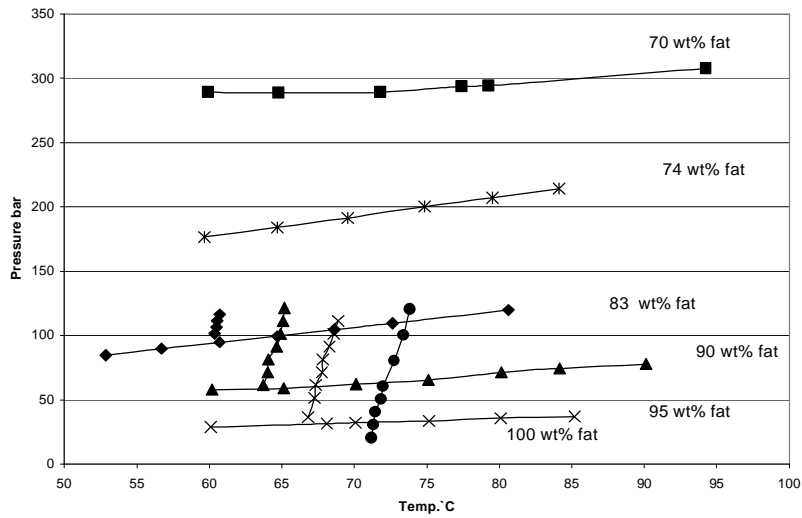


Figure1: P - T cross section of isopleths showing bubble-point curves (L+V? L), horizontal, and melting-point curves (S+L? L), vertical, for the binary system CO_2 + rapeseed 70.

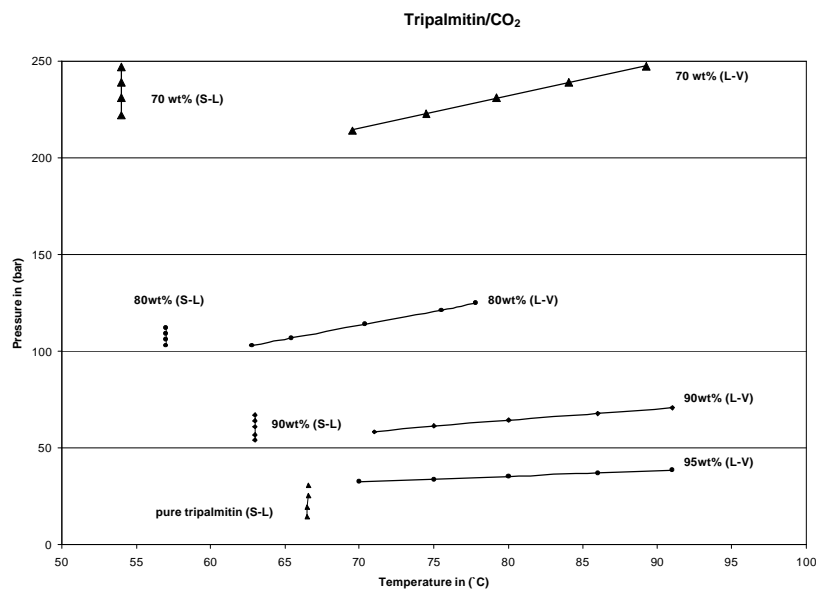


Figure2: P - T cross section of isopleths showing bubble-point curves (L+V? L), horizontal, and melting-point curves (S+L? L), vertical, for the binary system CO_2 + Tripalmitin.

Compared to the CO_2 + rapeseed system here, see Figure 2, lower bubble point pressures, in the range of 32-248 bar, are required to dissolve CO_2 in tripalmitin. Tripalmitin is a pure component what makes it different from rapeseed 70, which is a mixture of many different triglycerides of low percentages. The atmospheric melting range of rapeseed 70 in the absence of CO_2 lies between 40-70°C, while the melting point of tripalmitin is

sharply 67°C. Rapeseed 70 probably contains components in which the solubility of CO₂ is much lower than in the pure tripalmitin. In this respect one should realise that the melting-point and bubble-point curves do not represent sharp phase transitions but actually indicate the boundaries of transition zones.

The high purity of tripalmitin made it easier to get accurate L-V and S-L data. The point of intersection of the bubble-point curves and the solid solubility curves for a mixture of the same composition should give a point of the three phase curve solid fat + liquid + vapour, which starts in the triple point of the pure fat. According to Figures 1 and 2 this curve is found at temperatures higher than the critical temperature of pure CO₂ and shifts to high pressures. This makes it very likely that the CO₂ + fat system can be classified as a system with type III fluid phase behavior and a metastable liquid-liquid phase split [4,5].

Figure 3 gives the L-V and S-L phase behavior of the propane + rapeseed 70 system. As can be seen, relatively low pressures are needed to dissolve propane in rapeseed 70. Compared to the CO₂ + rapeseed and CO₂ + tripalmitin systems the highest pressure which was needed so far is only about 140 bar. Also the influence of the composition on the bubble-point pressure is much lower. What can be seen here clearly is that propane is more effective in terms of solvent capacity. Coorens et al., also found this for the propane + tripalmitin system [3].

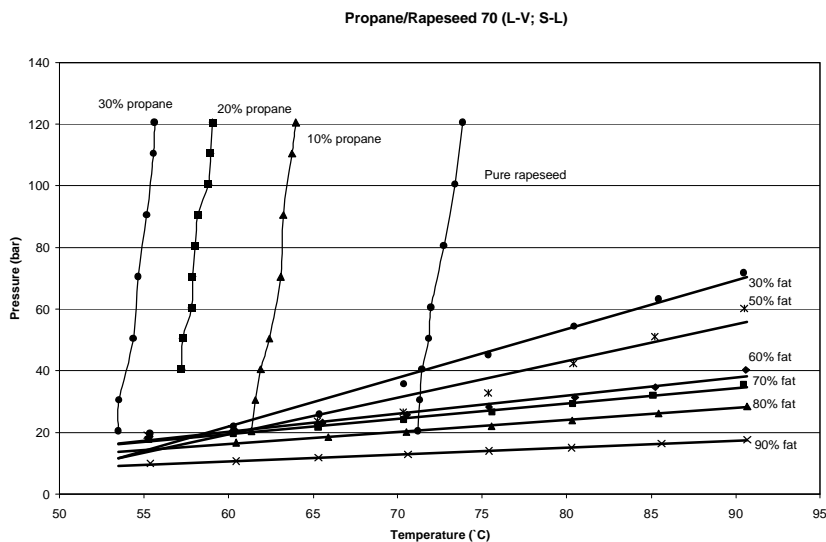


Figure 3: P-T cross section of isopleths showing bubble-point curves (L+V? L), horizontal, and melting-point curves (S+L? L), vertical, for the binary system propane + rapeseed 70.

Coorens et al. found that the system propane + tripalmitin behaves as a type IV system. Figure 4 represents the phase behavior of a mixture of 20wt% rapeseed 70 in propane. The figure shows a three-phase curve liquid-liquid-vapour and liquid-liquid lower solution temperature curve. This proves that the system propane + rapeseed 70 is also a type IV system.

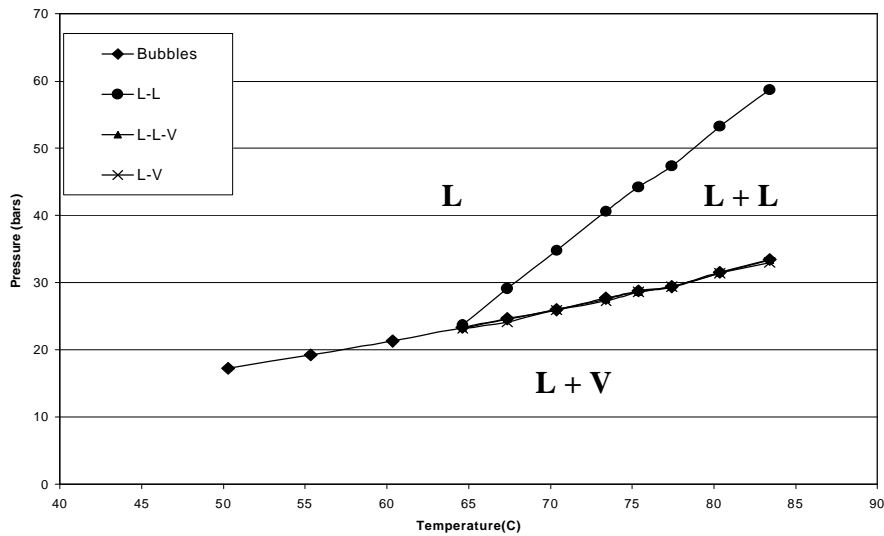


Figure4: P-T cross section of isopleths showing the L-L-V phase split for the binary system propane/rapeseed.

CONCLUSION

From the experimental results on the bubble point curves of CO₂ + fat and propane + fat systems it can be concluded that propane is a much better solvent for fats than CO₂. In order to dissolve propane in rapeseed 70 it is not needed to go to supercritical conditions of propane. For the CO₂ + rapeseed 70 system much higher pressures are needed to dissolve CO₂ than for CO₂ + tripalmitin.

The accuracy of the phase boundary pressures for the CO₂ + rapeseed 70 was ± 0.2 bar and for CO₂ + tripalmitin was ± 0.02 bar.

Experiments show that the systems CO₂ + rapeseed 70 and CO₂ + tripalmitin behave like a type III system with a metastable liquid-liquid phase split. For the system propane + tripalmitin a type IV system is observed in accordance with the classification of van Kyonenburg and Scott.

FUTURE OUTLOOK

In the near future a model from above mentioned data with Peng-Robinson EOS and the process development for particle formation of edible fats will be published.

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