

DETERMINATION OF SOLID-LIQUID-GAS EQUILIBRIUM CURVES FOR SOME FATS IN PRESENCE OF CARBON DIOXIDE

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Solid-Liquid-Gas equilibrium (S-L-G) curves have been investigated for different binary systems consisting of carbon dioxide and fats in order to determine the melting point depression caused by pressurized CO₂. The knowledge of the decrease of the melting points of the materials is important because different processes can be operated at reduced energetic costs.

The S-L-G diagrams for binary systems containing fats and carbon dioxide have been determined experimentally using the “first melting point” method. The compounds considered were some saturated fatty acids and triglycerides that are an ester combination of fatty acids with glycerol. The interest in this class of compounds was originated starting with the idea that impregnation processes could be easier and cheaper if under a low CO₂ pressure fats become liquid at temperatures close to the ambient temperature.

The Peng-Robinson equation of state with two binary interaction parameters was used to predict the thermodynamic behaviour of these systems and a comparison between the P, T experimental projections and the predicted curves was performed.

INTRODUCTION

The importance of considering the behaviour of fats, which are a long term energetic reservoir for a great part of the organisms, is clear due to their huge employment in food, pharmaceutical and cosmetic industries [1].

The interest in processing these materials with carbon dioxide was suggested by the features of this light compound. As a solvent, carbon dioxide is non-toxic, it can be purchased highly pure at cheap prices and it is suitable for processing thermolabile fat-soluble compounds.

The separation processes with pressurized fluids can be performed after the phase behavior determination of the involved systems. Usually the interest is in highly asymmetric binary systems consisting of a light solvent, the CO₂ in this case, and a heavier solid component whose melting temperature is higher than the critical temperature of the solvent [2].

The P, T diagram gives the possibility to easily understand the phase behavior of the analysed systems and to estimate the selectivity of the chosen solvent for the solid. In this work the experimental determination of the S-L-G curves has been performed in a visual cell using the “first melting point” method. This experimental approach was chosen because of its simplicity and quickness of operation [3], [4].

A thermodynamic model has been developed to predict the P, T projections of the studied binary systems: the model is based on the assumption that the solid phase does not contain the solvent and that the fugacity of the solid can be calculated as for a subcooled liquid [5], [6].

Under these conditions, indicating with 1 the solid and with 2 the solvent, the three phase equilibrium can be described by the following isofugacity equations:

$$x_1 \hat{\phi}_1^L P = y_1 \hat{\phi}_1^G P \quad (1)$$

$$x_2 \hat{\phi}_2^L P = y_2 \hat{\phi}_2^G P \quad (2)$$

$$f_1^S = x_1 \hat{\phi}_1^L P \quad (3)$$

in which x_i are the liquid compositions, y_i the compositions in the vapour phase, j_i^L and j_i^G the fugacity coefficients in the liquid and in the gas phases and f_1^S the fugacity of a sub cooled liquid that simulates the behaviour of the solid.

The fugacity coefficients have been calculated using the cubic equation of state of Peng-Robinson with two binary interaction parameters k_{ij} and l_{ij} .

I – MATERIALS AND METHODS

Materials

Four fatty acids (lauric, myristic, palmitic and stearic acid) and three triglycerides (trimyristin, tripalmitin and tristearin) were purchased from Sigma. In table 1 the characterising parameters, used for the correlation of experimental data and for the prediction of the P, T curves, are reported.

In the table T_f were experimentally determined, ΔH_f taken from Domalsky and Hearing [7], the fatty acids T_c and P_c obtained from D'Souza and Teja [8], the triglycerides T_c and P_c acquired from Weber [9] and the ω values calculated using the Lee-Kesler method.

Compound	T_f [K]	ΔH_f [KJ/mol]	T_c [K]	P_c [bar]	w
Lauric Acid	312.0	36.6	743.4	18.7	0.94
Myristic Acid	323.0	40.7	765.2	16.4	0.95
Palmitic Acid	330.0	54.8	785.2	14.7	1.0
Stearic Acid	337.0	61.3	805.1	13.3	1.1
Trimyristin	330.2	152.2	880.3	5.8	1.74
Tripalmitin	338.0	179.4	889.1	5.1	1.82
Tristearin	346.0	203.3	900.9	4.6	1.91

Table 1: Characteristic fat parameters.

Experimental Apparatus

The melting point depressions of the compounds have been determined with the so-called “first melting point” method by using the optical apparatus reported in figure 1.

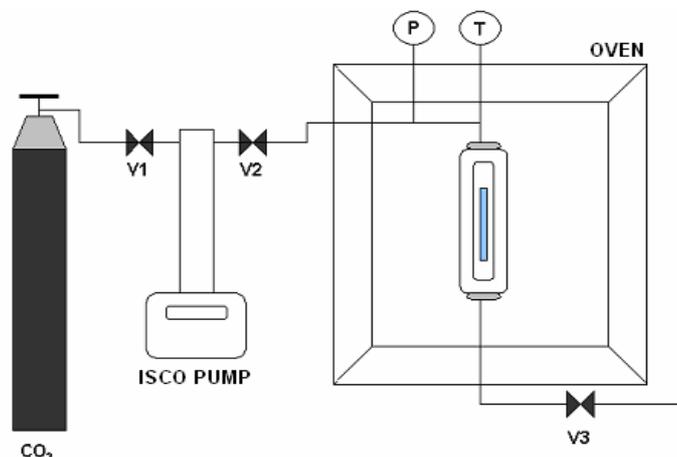


Figure 1: Experimental apparatus for the determination of the P, T curves. V1, V2 and V3 are two-ways valves; P identifies a pressure meter (Druck Instruments); T identifies a thermometer (Delta Ohm, HD 9214).

The optical system with an inner volume of about 100 cm^3 consists in a visual cell (Klinger), which contains a sample of about 0,4g of solid material. The view cell is placed in an oven, which is used to keep the temperature constant. An ISCO 260D syringe pump, working at constant pressure, introduces in the system the CO_2 flowing from the bomb.

The sample is placed in the cell at ambient pressure, afterwards the system is flushed with CO_2 in order to remove the air.

All the solid compounds were analysed under a CO_2 pressure of 100 bar because higher pressures would lead to high operative costs during the processes.

The melting points have been determined thermostating the system at the desired temperature and then adjusting the pressure until the solid begins to melt. The experimental determination of the data is strongly dependent on the observer and, as a consequence, every melting point has been repeated at least three times to guarantee enough accuracy.

II - RESULTS AND DISCUSSION

In figures 2 and 3 experimental and predicted P, T curves for the fatty acids and the triglycerides are reported. The predicted curves are determined, for all the systems, starting from the critical parameters of CO_2 and the data reported in table 1 for the solids, using the Peng-Robinson equation of state to calculate the fugacity coefficients in the liquid and gas phases. Binary interaction parameters k_{ij} and l_{ij} for the CO_2 -solid system have been obtained by fitting vapour-liquid equilibrium experimental data taken from literature [9], [10].

A linear relation between binary parameters k_{ij} and l_{ij} and the number of carbon atoms of the fatty acids was evidenced. The same kind of relation has been remarked between the slopes of the S-L-G curves and the number of the carbon atoms of each fatty acid (see figures 4 and 5).

The melting point experimental determinations of the triglycerides were more difficult than for the fatty acids: the latter infact can crystallize in different structures because of the long hydrocarbon chains in their molecules [11], [12]. The DSC technique is the most

effective tool to determine the polymorphic forms of a triglyceride and to study the aging phenomenon, which leads to the disappearing of the α -polymorphic phase with time [13].

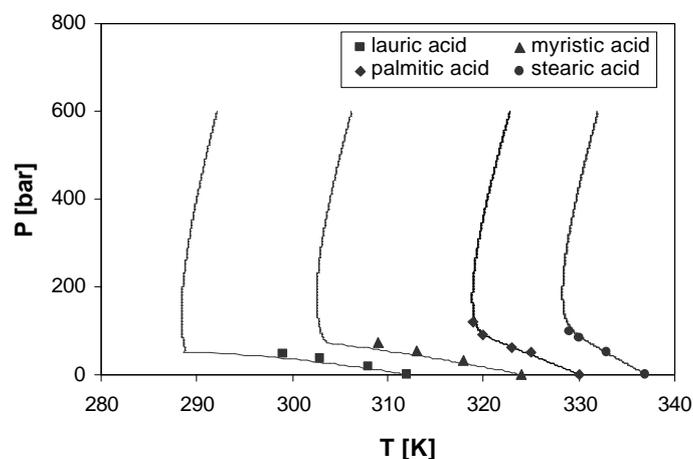


Figure 2: Experimental points and predicted (PR-EOS) S-L-G curves for fatty acids.

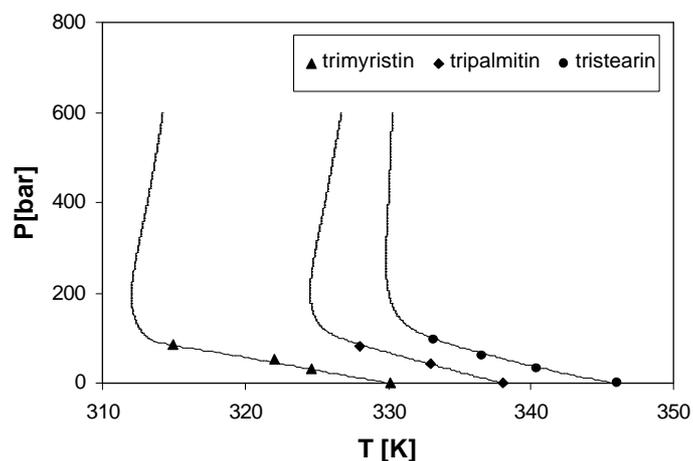


Figure 3: Experimental points and predicted (PR-EOS) S-L-G curves for triglycerides.

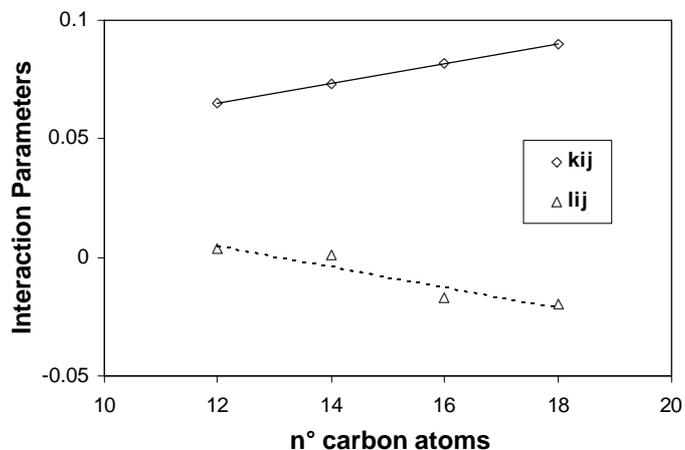


Figure 4: Binary interaction parameters (k_{ij} , l_{ij}), and number of carbon atoms for fatty acids.

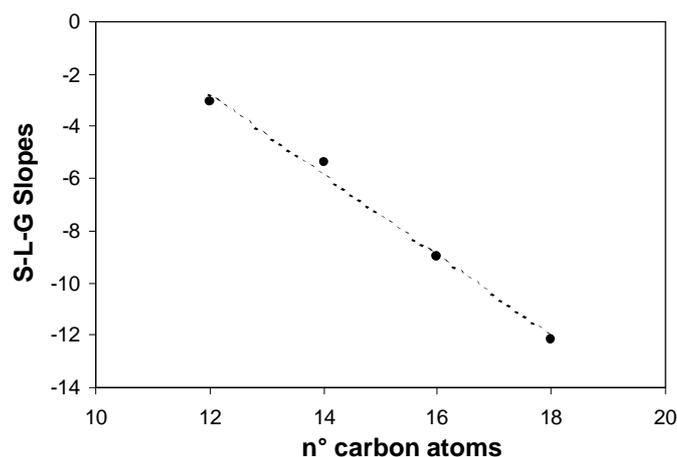


Figure 5: Slopes of the S-L-G curves and number of carbon atoms for fatty acids.

The time needed to charge the system and to take it to the desired operative conditions was high enough to assume that the triglycerides had aged and to obtain the melting point depressions reported in figure 3. This assumption was checked with differential thermal analysis on solid froze samples and on the same samples left at ambient temperature for 2 hours. The DSC behaviour for tristearin is reported in figure 6.

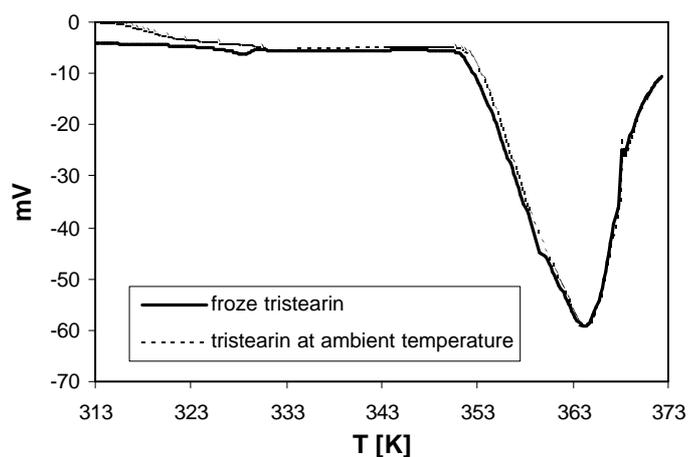


Figure 6: DSC for tristearin.

CONCLUSION

In this study the influence of pressurized CO_2 on the melting point of some fats was investigated by means of an optical system using the “first melting point” method. It has been possible to notice experimentally that using pressurized CO_2 a melting point reduction of at least 10K degrees can be reached for all the compounds.

A prediction of the P, T projections has been achieved using the cubic equation of state of Peng-Robinson. A good agreement between the calculated and the experimental data has been evidenced.

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