

PHASE EQUILIBRIA OF OLEIC, PALMITIC, STEARIC, LINOLEIC AND LINOLENIC ACIDS IN SUPERCRITICAL CO₂

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Abstract - The knowledge of the phase equilibrium is one of the most important factors to study the design of separation processes controlled by the equilibrium. Fatty acids are present in high concentration as by-products in vegetable oils but the equilibrium data involving these components is scarce. The objective of this work is the experimental determination of the liquid-vapor equilibrium of five binary different systems formed by carbon dioxide and palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3). The equilibrium experimental data was collected at 40, 60 and 80°C at 60, 90 and 120 bar, at the extract and raffinate phases, using an experimental apparatus containing an extractor, a gas cylinder and pressure and temperature controllers. The data was modeled using the cubic equation of state of Peng-Robinson with the mixing rule of van der Waals with binary interaction parameters. The model was adequate to treat the experimental data at each temperature and at all the temperatures together. The best model that includes the van der Waals mixing rule with two parameters has maximum deviation of 17%. The distribution coefficients were also analyzed and it was concluded that the fractionation of the fatty acids is possible using supercritical carbon dioxide.

Keywords: Fatty acids; Equilibrium data; Supercritical extraction; Carbon dioxide.

INTRODUCTION

The supercritical extraction is considered an alternative technology due to the problems encountered in the separation step of the chemical processes. Besides, the design of this technology concerns because of the high cost of the total investment and the high pressures which are applied (Brennecke and Eckert, 1989).

The acknowledgment of the behavior of the phase equilibrium is of extreme importance for all the chemical processes and separation operations, mainly for the processes that occur at high pressures, since small pressure deviations may cause big project errors, a wrong choice of operation conditions or of the equipment dimensions. Moreover, the equilibrium data gives information about

the solvation power of the solvent, the quantity of solvent that dissolves in the liquid phase and about the composition of the phases in equilibrium, the selectivity of the solvent, the property changes with temperature and pressure and the extension of the region of equilibrium of two phases that is the limit condition of the supercritical extraction process.

Thus, the measurement of the equilibrium data is very important but difficult and of high cost, justifying the increasing use of thermodynamic models that have the capacity to represent those behaviors. Moreover, it is necessary a minimum number of experimental points to predict the representative parameters of each model and each studied system (Dohrn and Brunner, 1995).

According to Simões and Brunner (1996), two processes are traditionally employed in the

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desacidification: the chemical refining or desacidification by neutralization or treatment of the extracted oil with caustic soda solution, and the physical refining or desacidification by distillation, that consists on the separation of fatty acids and triglycerides based on their different boiling points. This process occurs at elevated temperatures and reduced pressures, and in those conditions the fatty acids are highly corrosive causing many problems to the equipment. Moreover, the energy cost is high because of the vapor production and also there is degradation of the components sensible to high temperatures. Some alternative processes like liquid-liquid extraction, with 98% of methanol, and the distillation with vapor, were studied and analyzed. The fatty acids extracted with methanol were of a good quality, although this method was applied in a small range of fatty with high rates of free fatty (Simões and Brunner, 1996). The use of supercritical carbon dioxide in the desacidification of olive oil and soybean and Brazil nut oils (Penedo and Coelho 1997^a, 1997^b, 1998) was also studied. The solubilities were compared in different conditions of temperature and pressure, under supercritical extraction, and the results indicated that the technology may be used.

Recent studies have investigated the modeling of the binary systems oleic acid/CO₂ and linoleic acid/CO₂, and of their esters (Zou et al., 1997; Yu et al., 1992; Yu et al., 1993). Espinosa et al. (2002) utilized group contribution methods and equations of state to determine the phase equilibrium in systems containing fatty acids. Following the same idea, Jaubert et al. (2001) compared the experimental results of extraction of EPA and DHA, sterified in supercritical carbon dioxide, with data obtained from group contribution methods. Some equations of state were also applied to represent phase equilibrium data of triglycerides in supercritical carbon dioxide (Florusse et al., 2002, 2004).

The most used models for systems at elevated pressures utilize the equation of state of Peng-Robinson (1976) to represent the liquid-vapor equilibrium or equations to represent the kinetic behavior (Sovová, 1994), presenting a good representation of a wide variety of systems with supercritical fluid. No general theory has been developed to represent an appropriate mixing rule, except for the case of the Virial equation of state (Stoldt and Brunner, 1998). In the last years, the capacity to model multiphase equilibrium data has increased significantly with the development of new types of empirical mixing rules (Johnston et al., 1989). The binary interaction parameters present in the equations of state and of extreme influence in the correlation of phase equilibrium data, varied with

temperature, pressure, density and composition (Jungfer and Brunner, 1999).

Due to the scarcity of phase equilibrium data of fatty acids necessary for the fractionation of them, the purpose of this work is to measure the equilibrium data of five binary systems of fatty acids (C16:0, C18:0, C18:1, C18:2 e C18:3) in supercritical carbon dioxide. The data was modeled with the Peng-Robinson equation of state and the classical mixing rule of van der Waals with two parameters. The distribution coefficients were calculated to predict the best operational conditions to separate them from the vegetable oils.

Literature Review

The phase equilibrium data necessary to determine the optimum operational conditions for desacidification is sometimes scarce. From all the fatty acids of interest in this work, the oleic acid is the fatty acid that has major experimental data.

Yu et al. (1992) developed a static method with recirculation to measure equilibrium data for the system CO₂ – oleic acid at 40 and 60°C and from 30 to 310 bar of pressure. Lockemann (1994) measured data of the same system at 40 and 50°C and pressures up to 80 bars. The liquid phase compositions are disposable, but the vapor phase cannot be visualized. These data can also be observed for the oleic and linoleic acids at 40 and 60°C for pressures up to 300 bar (Zou et al., 1990). Bharath et al. (1992) also measured the phase equilibrium data for the system CO₂-oleic acid at 40, 60 and 80°C for pressures between 100 and 300 bars. In 1993, Bharath et al. studied the behavior of the system CO₂-palmitic acid at 80 and 100°C at pressures from 130 to 305 bars.

Chen et al. (2000) measured liquid-vapor equilibrium data for the system CO₂-linoleic acid in the range of 40 to 60°C at pressures up to 241.2 bars. At constant density, the solubility increases with increasing temperature. At constant temperature, the solubility increases with the increase of the CO₂ density.

Vasconcellos and Cabral (2000) used the equation proposed by Chrastil (1982) to correlate the solubilities of fatty acids (oleic and linoleic acids), estimating the parameters of this equation that represent this family of compounds. The results show that the parameters present a linear behavior with the increase of the molecular weight then; the contribution group methods can be applied to estimate these parameters. Following this methodology, new solubility data can be predicted using the contribution group methods.

Saito et al. (2004) presented the equilibrium data modeling of the binary systems involving carbon

dioxide and the oleic, palmitic and linoleic acids at 60, 70, 80 and 90°C. The disadvantage is the absence of presentation of the experimental data.

In front of the scarcity of the equilibrium data involving these fatty acids, this work aims to contribute measuring the liquid-phase equilibrium and proposing a thermodynamic modeling of the experimental data, identifying the behavior of the distribution coefficients in function of the pressure and temperature.

MATERIALS AND METHODS

Materials

Standard samples of fatty acids from MERCK S.A. and carbon dioxide from AGA S.A with 99.99% of minimum purity were used.

Experimental Procedure

Firstly, the fatty acids were weighed before being fed into the extractor. This is necessary to know the exact quantity of fatty acids for the posterior quantification by gas chromatography. After feeding the raw material into the extractor, the unit was

closed and only the carbon dioxide entry valve was opened. After the addition of gas to reach the desired pressure, the unit was maintained at constant agitation and the heating was turned-on. The system was maintained under agitation for 30 minutes to assure a homogeneous mixture with perfect mass and heat exchanging. After that, the agitation system was turned-off to allow phase separation inside the extractor.

The extract and raffinate phases were collected in glass tubes under vacuum, immersed in an ice bath. After the separation of the fatty acids from the carbon dioxide, the volume of the gas was measured. The condensed solute present in the wall was weighed and transferred with the help of 1 to 2 ml of hexane for methylation (Hartman and Lago, 1973), necessary for the chromatographic analysis. The operational conditions of the chromatograph are shown in Table 1.

The experimental flow sheet of the unit can be seen in Figure 1. The operational conditions used were temperatures of 40, 60 and 80°C and applied pressures of 60, 90 and 120 bar.

More information about the experimental methodology and the experimental flow sheet of the unit can be found in Fortes (1996) and Fortes and Coelho (1995).

Table 1: Operational conditions of the chromatograph

Column temperature	190°C
Injector temperature	240°C
Detector temperature	250°C
N ₂ flow rate	50 ml/min
H ₂ flow rate	50 ml/min
Synthetic air flow rate	400 ml/min
Attenuation	10 mA
Column height	1.8m
Column diameter	3/16"
Stainless steel column	Packed with DEGS (17% in Cromosorb – W80/100 mesh)
Volume of sample injected	3 to 10µl

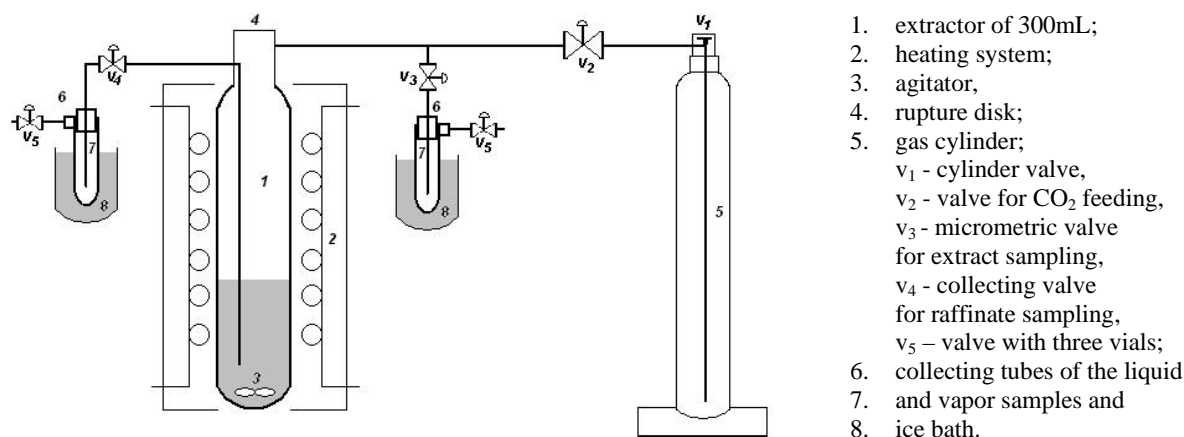


Figure 1: Extraction unit with FSC

Thermodynamic Modeling

The study of the thermodynamic modeling of the systems involving the fatty acids and the carbon dioxide is characterized by the liquid-supercritical fluid equilibrium. For the phase equilibrium calculation, the “ ϕ - ϕ ” methodology is utilized. In this approach, the two phases are represented by an equation of state in a wide range of temperatures and pressures and because the high pressure equilibrium does not involve chemical reactions neither electrolytes.

Due to the explained conditions, the fugacity criterion for the liquid-vapor equilibrium is expressed as

$$\hat{f}_i^l = \hat{f}_i^g \quad (1)$$

The same expression can be written as a function of the fugacity coefficients for the two phases

$$x_i \phi_i^l = y_i \phi_i^v \quad (2)$$

The fugacity coefficients were calculated using the Peng-Robinson (1976) equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (3)$$

with

$$a = a_{ci} \cdot \alpha(T, w) \quad (4)$$

where a_{ci} can be calculated for the pure components by the following relations

$$a_{ci} = 0,457224 \cdot \frac{(R \cdot T_{ci})^2}{P_{ci}} \quad (5)$$

$$b_i = b_{ci} = 0,07780 \frac{RT_{ci}}{P_{ci}} \quad (6)$$

$\alpha(T, w)$ is a function responsible for showing the dependence of the attractive parameter with the temperature, T_c and P_c are the critical temperature and pressure, respectively, V is the total volume of the system, T is the temperature and R is the gas constant. There are different functions proposed in the literature, but in this work the function proposed by Almeida et al. (1992) was used

$$\alpha(T) = \exp \left[m(1 - T_r) |1 - T_r|^{\Gamma-1} + n(T_r^{-1} - 1) \right] \quad (7)$$

m , n and Γ are parameters obtained by the vapor pressures of the pure components. In this case, the vapor pressures, for all the fatty acids, were predicted using the Wagner-Vetere method (Poling et al., 2001). The equation of Almeida et al. (1992) was selected by the research group because of its good correlation with other types of solutes (Mendes, 2002; Melo, 1999).

Due to the positive results found by the research group for a large number of different binary systems involving the supercritical carbon dioxide, the thermodynamic modeling still includes the classical mixture rule of Van der Waals with two parameters:

$$a_m = \sum_i \sum_j z_i z_j a_{ij}, \quad a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (8)$$

$$b_m = \sum_i \sum_j z_i z_j b_{ij}, \quad b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (9)$$

where k_{ij} and l_{ij} are the adjustable binary interaction parameters.

The interaction parameters were estimated according to the computational program developed by Pinto et al. (1987), involving liquid-vapor experimental equilibrium data. This parameter estimation method is based on the Maximum Likelihood Method minimizing the following objective function

$$FO = \sum_{i=1}^{NP} \frac{(y_i^{cal} - y_i^{exp})^2}{\sigma_{y_i}^2} + \sum_{i=1}^{NP} \frac{(P_i^{cal} - P_i^{exp})^2}{\sigma_{P_i}^2} \quad (10)$$

with $(\sigma_y)_i$ and $(\sigma_p)_i$ as the experimental deviations of the vapor molar fraction and of the total pressure of the system, respectively, and y_{exp} and y_{calc} are the compositions of the experimental and calculated vapor molar fractions, as P_{exp} and P_{calc} are the experimental and calculated total pressures of the system, respectively.

The thermodynamic calculation was based on the bubble point algorithm, with temperature and liquid molar fraction of the carbon dioxide as specified variables to calculate pressure and vapor molar fractions of the solvent. The calculated variables (total pressure and vapor molar fraction) were

compared with the experimental values through the medium deviation using the following relations

$$AAD = \sum_i^{NEXP} \frac{(P_{exp} - P_{calc})}{P_{exp}} \bigg/ NEXP \quad \text{and} \quad (11)$$

$$AAD = \sum_i^{NEXP} \frac{(y_{exp} - y_{calc})}{y_{exp}} \bigg/ NEXP$$

where NEXP are the experimental data points used in the parameters estimation.

Critical Properties

The thermodynamic relations used to describe the phase equilibrium need some critical and physicochemical properties. The most important are the critical temperature (T_c) and pressure (P_c) and

the acentric factor (w). Table 2 shows critical temperature and pressure, calculated by the Joback model described in Poling et al. (2001) and the acentric factor, predicted by the Wagner-Vetere equation (Poling et al., 2001), together with the parameters necessary to calculate the vapor pressures.

RESULTS AND DISCUSSIONS

The results of the molar fraction of CO₂ for the extract and raffinate phases are presented in Tables 3 and 4, respectively. Although other works have studied the equilibrium at higher pressure conditions, compositions of CO₂ in equilibrium with the fatty acids are shown in the tables. These results represent a chance to predict and simulate a process of separation or concentration of fatty acids at lower conditions of temperature and pressure.

Table 2: Critical properties for all the fatty acids studied

Properties	*CO ₂	C16:0	C18:0	C18:1	C18:2	C18:3
T _c (K)	304.1	780.4	796.7	796.3	796.0	959.5
P _c (bar)	73.8	14.67	13.25	12.42	12.40	13.7
W	0.239	1.010	1.086	0.924	0.776	0.959

*Poling et al. (2001)

Table 3: Molar fractions of CO₂ for the extract phase, for each binary system investigated

Extract phase						
P (bar)	C16:0	C18:0	C18:1	C18:2	C18:3	
T = 313.15 K						
60	0.9980	0.9992	0.9965	0.9929	0.9984	
90	0.9954	0.9992	0.9950	0.9905	0.9979	
120	0.9939	0.9991	0.9939	0.9893	0.9970	
T = 333.15 K						
60	0.9984	0.9992	0.9969	0.9938	0.9985	
90	0.9960	0.9992	0.9956	0.9908	0.9980	
120	0.9949	0.9991	0.9941	0.9899	0.9975	
T = 353.15 K						
60	0.9985	0.9996	0.9969	0.9943	0.9985	
90	0.9965	0.9992	0.9957	0.9914	0.9980	
120	0.9950	0.9992	0.9946	0.9905	0.9979	

Table 4: Molar fractions of CO₂ for the raffinate phase, for each binary system investigated

Raffinate phase						
P (bar)	C16:0	C18:0	C18:1	C18:2	C18:3	
T = 313.15 K						
60	0.9347	0.9871	0.8945	0.8388	0.9892	
90	0.9494	0.9915	0.9223	0.8738	0.9931	
120	0.9562	0.9924	0.9370	0.8887	0.9939	
T = 333.15 K						
60	0.9282	0.9857	0.8808	0.8231	0.9881	
90	0.9443	0.9887	0.9132	0.8609	0.9905	
120	0.9523	0.9919	0.9336	0.8792	0.9936	
T = 353.15 K						
60	0.9197	0.9818	0.8689	0.8077	0.9844	
90	0.9405	0.9879	0.9057	0.8522	0.9899	
120	0.9473	0.9894	0.9254	0.8665	0.9911	

The calculation of the thermodynamic equations to represent the experimental data was done using the bubble point methodology. Because of the low number of experimental data for each temperature (three pressures were investigated), the parameters estimation was done using all the conditions of temperature and pressure with a total of nine experimental points, for each binary system investigated. The parameter estimation at constant temperature was not successful because of the low number of points.

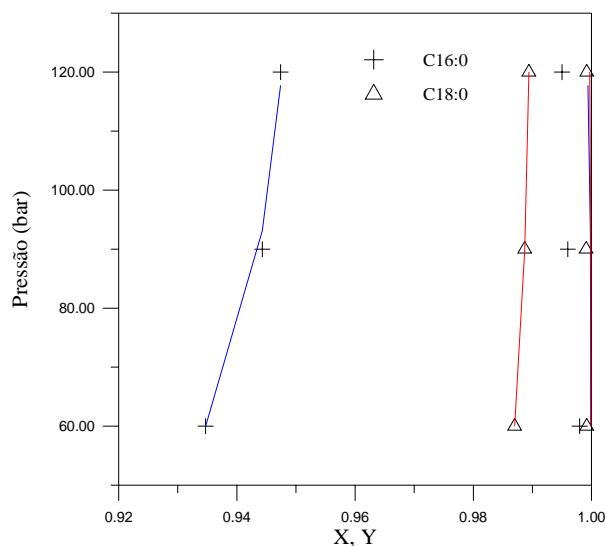


Figure 2: Experimental and calculated liquid-vapor equilibrium data for the binary systems $\text{CO}_2\text{-C16:0}$ and $\text{CO}_2\text{-C18:0}$

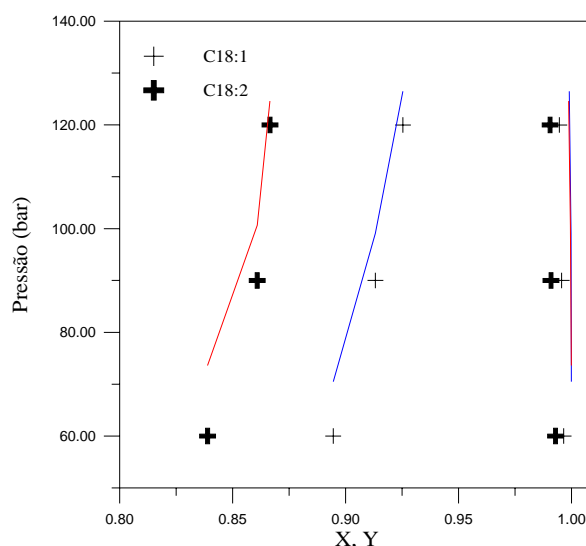


Figure 3: Experimental and calculated liquid-vapor equilibrium data for the binary systems $\text{CO}_2\text{-C18:1}$ and $\text{CO}_2\text{-C18:2}$

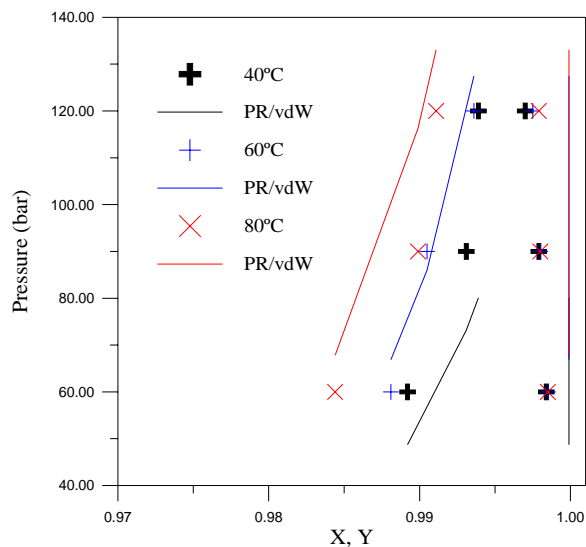


Figure 4: Experimental and calculated liquid-vapor equilibrium data for the binary system $\text{CO}_2\text{-C18:3}$

Figure 2 shows the behavior of the model, represented by the dashed lines, in comparison with the experimental data of the binary systems, $\text{CO}_2\text{-C16}$ and $\text{CO}_2\text{-C18:0}$, and Figure 3 for the systems $\text{CO}_2\text{-C18:1}$ and $\text{CO}_2\text{-C18:2}$, involving the three studied temperatures. Equilibrium data for the $\text{CO}_2\text{-C18:3}$, binary system, are presented in Figure 4 for all the temperatures investigated. Comparing the three figures, it can be observed that the last system was not well represented at 40°C , but the behavior of the model improved for higher conditions of temperature.

These different behaviors presented by the binary systems can be better understood by the values of the deviations in relation to the total pressure and vapor phase composition of CO₂ shown in Table 5. The pressure deviations were higher for the binary system that involves C18:3 because of the behavior of the model for the temperature of 40°C.

Table 6 shows the binary parameters estimated using all the experimental data for each binary system. This methodology makes possible to use these parameters to predict new phase equilibrium data at the same range of temperatures and pressures.

The deviations encountered in this work were smaller than those reported by different authors (Zou et al., 1990; Yu et al., 1992, 1993). The deviations were calculated based on a program depending on an objective function containing the variables pressure

and vapor phase composition. Perhaps the difference among the deviations results from different objective function adopted by the authors, depending on the compositions of the liquid and vapor phases. This methodology minimizes the deviations due to the fact that pressure is one of the most important variables in the project of supercritical fluid extraction.

Because of the good representation of the model for all the studied systems, Figures 5, 6, 7, 8 and 9 show the predicted equilibrium curves at 40, 60 and 80°C, calculated using the estimated parameters, for all the binary systems investigated.

The equilibrium curves for the system carbon dioxide-oleic acid (CO₂-C18:1), presented in Figure 7, have the same behavior of the curves presented in the literature (Lockemann, 1994; Bharath et al., 1993).

Table 5: Medium absolute deviations for the total pressure and vapor phase compositions for all the systems investigated

Fatty Acids	AADP (%)	AADY (%)
C16:0	1.83	0.87
C18:0	0.03	4.63
C18:1	10.99	0.04
C18:2	12.78	0.80
C18:3	16.22	0.19

Table 6: Binary interaction parameters estimated for each binary system

Fatty Acids	K _{ij}	L _{ij}
C16:0	0.0254	-0.3724
C18:0	0.0266	0.2852
C18:1	0.0099	-0.2042
C18:2	0.0583	-0.2236
C18:3	-0.0437	-0.8999

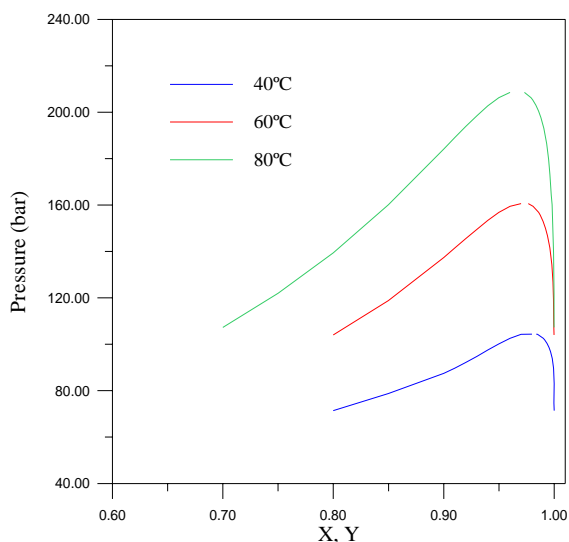


Figure 5: Equilibrium curve for the binary system CO₂-C16, at 40, 60 and 80°C

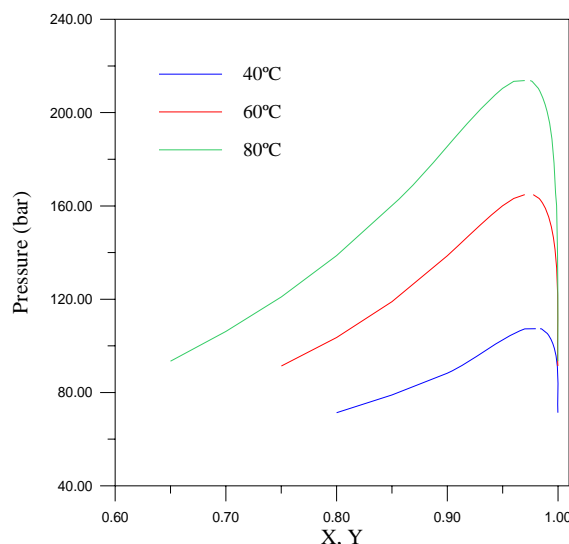


Figure 6: Equilibrium curve for the binary system CO₂-C18, at 40, 60 and 80°C

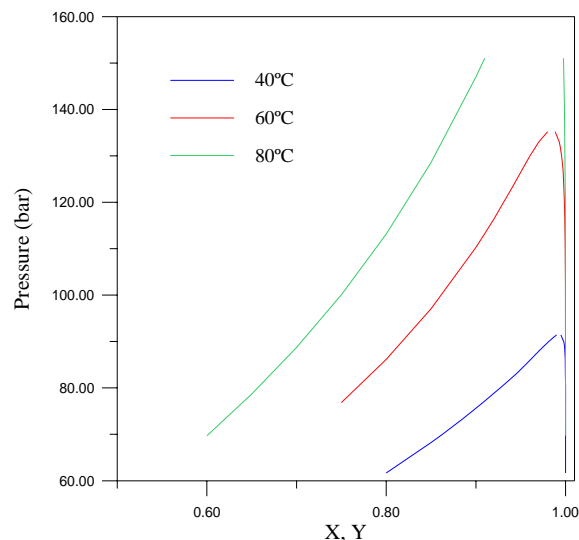


Figure 7: Equilibrium curve for the binary system CO_2 -C18:1, at 40, 60 and 80°C

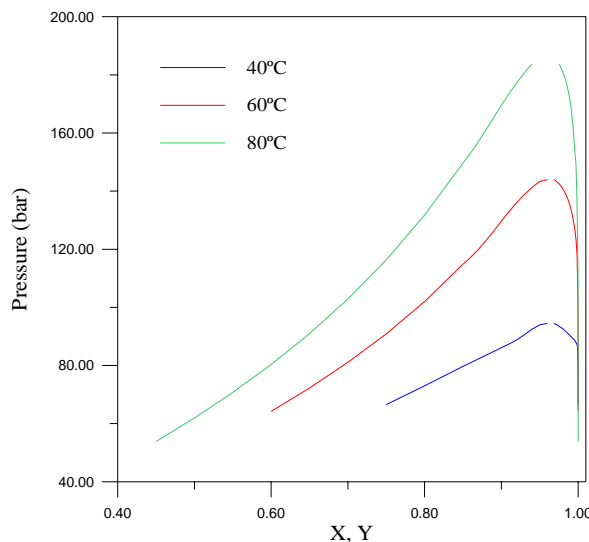


Figure 8: Equilibrium curve for the binary system CO_2 -C18:2, at 40, 60 and 80°C

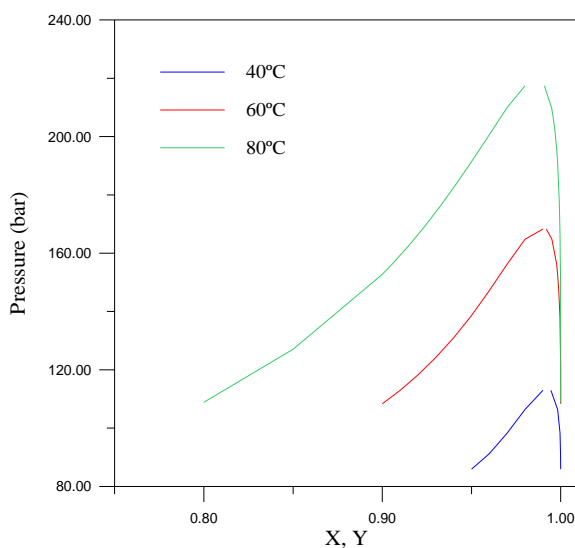


Figure 9: Equilibrium curve for the binary system CO_2 -C18:3, at 40, 60 and 80°C

Because of the different operational conditions studied for the binary systems, the better system to compare the experimental data is CO_2 – linoleic acid (C18:2), from the work of Chen et al. (2000), presented in Figures 10 and 11, for the temperatures of 313.15K and 333.15K. The results from Chen et al. (2000) show a good agreement with those obtained in this work, confirming the experimental methodology adopted.

Another binary system, CO_2 – oleic acid was compared with two other works published in the literature and it was observed that this system had the major deviation between the data, mainly in the

liquid phase. This can be observed in Figure 12. Although the deviation was higher between the data, the experimental data of this work had a lower deviation compared to Bharath et al. (1992).

Other experimental data presented in the literature could not be compared to our data because of the different operational conditions applied and because of the nature of the data. Some data are only expressed in terms of the solubility, like palmitic acid (Ohgaki et al., 1989).

In general, the solubility of CO_2 in the liquid phase did not change much with increasing temperature. The solubility of each heavy compound

in the vapor phase increases with increasing pressure, which also increases the K values (distribution coefficients). This fact was also reported by Chen et al. (2000).

The results indicate that the distribution coefficients for all the fatty acids increase with increasing temperature and pressure. The lower K values were obtained for oleic and linolenic acids at

40°C. The higher values were for palmitic and linoleic acids at 80°C. Figure 13 presents the distribution coefficients of the fatty acids as a function of pressure at 80°C.

Due to the fact that the equilibrium data of the binary systems were measured at lower conditions of temperature and pressure than the other works, Figure 13 compares all the equilibrium data involved.

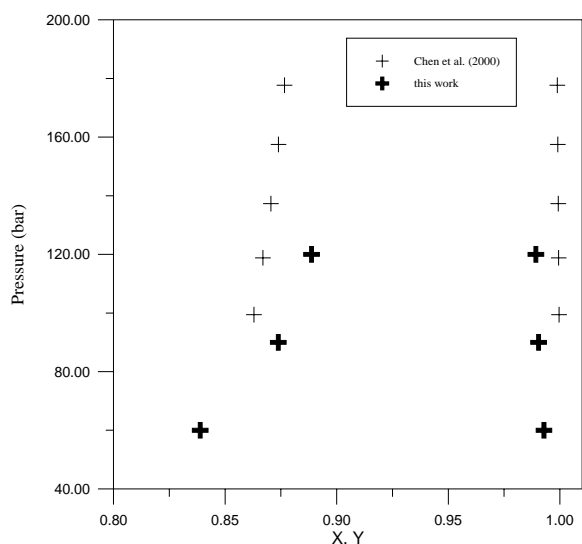


Figure 10: Comparison of the liquid-vapor equilibrium data of CO₂-linoleic acid at 313.15K

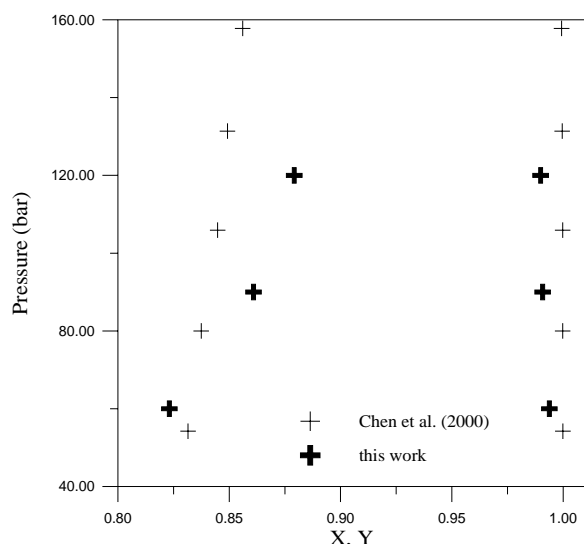


Figure 11: Comparison of the liquid-vapor equilibrium data of CO₂-linoleic acid at 333.15K

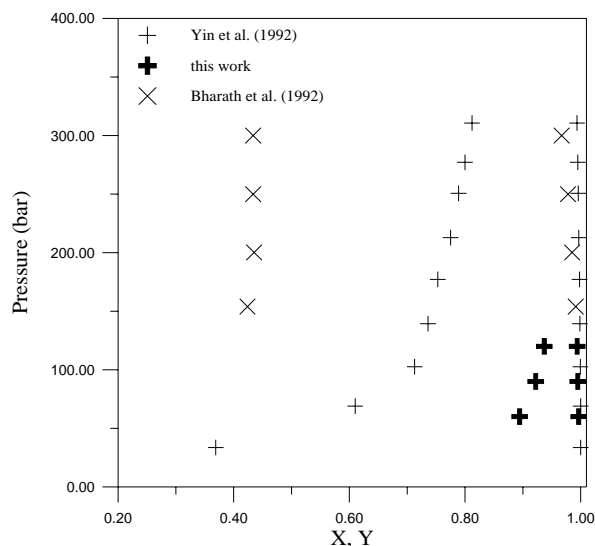


Figure 12: Comparison of the liquid-vapor equilibrium data of CO₂-oleic acid at 313.15K

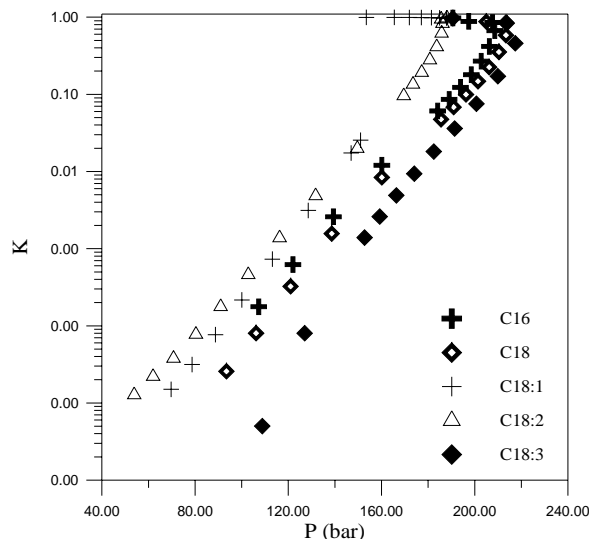


Figure 13: Distribution coefficients at 80°C

CONCLUSIONS

Phase equilibrium studies demonstrated the efficiency of the equipment device for vapor and liquid phases. In this study the binary liquid-vapor equilibrium data was measured for systems of carbon dioxide + C16:0, carbon dioxide + C18:0, carbon dioxide + C18:1, carbon dioxide + C18:2 and carbon dioxide + C18:3. The operational conditions investigated varied from 40 to 80°C and from 60 to 120 bars. Experimental results indicated that the mole fraction of carbon dioxide in the liquid phase was very high even at low pressure and rather low in the vapor phase.

The experimental data was correlated by a thermodynamic model containing two binary interaction parameters. They were predicted for all the temperatures together. The model represented well the experimental data for the different fatty acids, except at 40°C for the system carbon dioxide + linolenic acid. Based on this result, equilibrium curves were calculated for all the binary systems investigated and it was observed that the distribution coefficients increase with increasing temperature. This fact proves that the separation of the fatty acids using supercritical carbon dioxide is technically promising.

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