High-Pressure Solubility Data for Palm Oil−SF_6 and Coconut Oil−SF_6 Systems

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High-pressure vapor−liquid-phase equilibria ($P-T-x-y$) for the palm oil−SF_6 and coconut oil−SF_6 systems were investigated at temperatures of (313.15 and 333.15) K in the pressure range from (1 to 50) MPa. The phase behavior of two vegetable oils in sulfur hexafluoride (SF_6) was studied using an isothermal−analytical method in combination with a visual-synthetic method using a variable-volume cell. For both systems, at the lower investigated temperature of 313.15 K, the transition from a two-phase system to a three-phase system was observed visually under conditions near the phase transition of SF_6 from a vapor to a liquid phase. Moreover, the phase inversions for the vegetable oil−SF_6 systems were also recorded at both temperatures under investigation.

Introduction

Vegetable oils represent a very important market, not only for human or animal nutrition but also for biochemical and bioenergy production.[1] Even though the main constituents are triglycerides, vegetable oils also contain both mono- and diglycerides, free fatty acids, phospholipids, glycolipids, sterols, and other fat-soluble components including tocopherols, tocotrienols, carotenoids, and squalene which are important as pharmaceutical and food additives.[2] Vegetable oils, in general, have excellent properties such as high viscosity index, high lubricity, low evaporative loss, high biodegradability, and low toxicity with regard to their use as bases for lubricants. On the negative side, they are known to possess low thermal, oxidative, and hydrolytic stabilities.[3] The difference in the number of unsaturated bonds of the fatty acid molecules characterizes the physical and nutritive properties of vegetable oils.

Palm oil and coconut oil are two of the most important oil crops in tropical regions.[4] Coconut oil belongs to a unique group of vegetable oils called "lauric oils". The most abundant fatty acid in this group is lauric acid, and more than 90 % of the fatty acids of coconut oil are saturated.[3] Palm oil is a semisolid fat at room temperature and can easily be separated into two fractions by partial crystallization in a liquid phase. It is widely used in various food products, such as margarines, cooking oils, and confectionery fats.[5] The major fatty acids of palm oil are palmitic and oleic acids.[6] The chemical compositions of palm and coconut oils can be found in the literature.[3−6]

The food industry is always looking for the best separation technology to obtain natural compounds of high purity and healthy products having excellent qualities.[7] The high cost of organic solvents, increasingly stringent environmental regulations, and the new requirements of the medical and food industries for ultrapure products have increased the need for development new and clean technologies for the processing of food products.[8] Therefore, the design of new products with special characteristics or new, environmentally friendly processes is significant challenge for chemical engineers.[9]

Considerable interest has been shown in the development of supercritical fluid processing in the oil and fat industries.[10] Vegetable oil solubility data in supercritical fluids are crucial together with knowledge about the influence of pressure and temperature on the equilibrium. Carbon dioxide (CO_2), as a high-pressure liquid solvent for vegetable oils including palm oil, has been extensively studied in previous works,[11−21] due to the fact that it is a clean, nonflammable, and nontoxic solvent.[21] On the other hand, phase equilibrium investigations on vegetable oil−CO_2 systems have shown that carbon dioxide has low solvent power in the case of vegetable oils. The vegetable oil solubility in CO_2 is low, even at pressures as high as 30 MPa. Therefore, the extraction of oils from vegetable matrices using CO_2 is not very attractive from an economic point of view.[22]

Sulfur hexafluoride (SF_6) as a high-pressure solvent shows a generally higher solvent power for sunflower oil and soyabean oil.[23] Therefore, SF_6 opens new perspectives as a high-pressure liquid solvent.

In the present research, phase equilibrium data of palm and coconut oils in SF_6 were measured at temperatures of (313.15 and 333.15) K and at pressures up to 50 MPa. Phase equilibrium data for the above-mentioned systems could not be found in the literature. Additionally, the obtained experimental results were compared with solubility data for sunflower and soyabean oil in SF_6, obtained at 313.15 K.[23] Moreover, the contents of saturated and unsaturated fatty acids in sunflower, soyabean, palm, and coconut oils were determined by GC analyses and the phase equilibria measurements then discussed regarding the chemical compositions of the oils.

Experimental Section

Materials. Palm oil (Cat. No-70905) was supplied by Fluka (Germany). Coconut oil (Cat. No-C 1758) was provided by Sigma-Aldrich (Cat. No-95682). SF_6 was obtained from Linde plin (Celje, Slovenia) with guaranteed purity in mass fraction higher than 0.999.

Phase Equilibrium Determination. The determination of phase equilibrium data for palm oil−SF_6 and coconut oil−SF_6 systems was performed using a variable-volume view cell apparatus (Figure 1). A detailed description of the apparatus and method can be found in the literature.[23] The apparatus consists of a high-pressure variable-volume view cell (NWA GMBh, Lorrach, Germany), which is designed for a pressure

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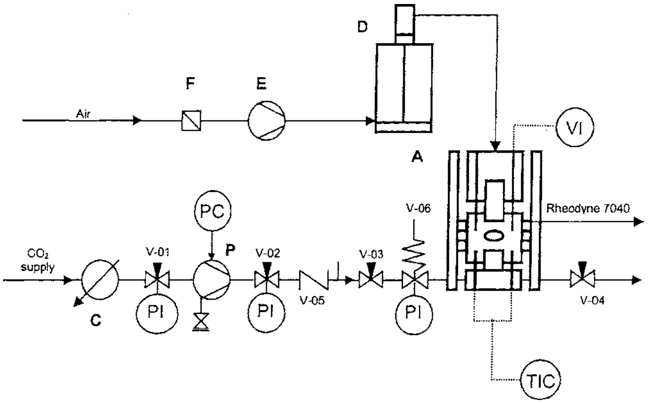

Figure 1. Shematic of equilibrium cell apparatus: A, variable-volume view cell; C, cooler; D, hydraulic oil system; E, air compressor; F, filter; P, high-pressure membrane pump; V01−04, high-pressure needle valves; V05, one-way valve; V06, safety valve; PI, pressure indicator; VI, voltage indicator; PC, pressure controller; TIC, temperature indicator controller.

of 75 MPa and temperature of 473.15 K, with a variable volume between (30 and 60) mL. The isothermal-analytical method in combination with the visual-synthetic method was used for phase behavior determination. During sampling, the observed pressure change was up to 1.5 MPa, while the temperature was constant.

Analytical Determination of Saturated and Unsaturated Fatty Acids. Saponification. Free fatty acid (FFA) was prepared by the saponification of vegetable oils.[24] A NaOH solution was prepared by dissolving 48 g of NaOH and 0.5 g of Na_2EDTA in 160 mL of water. Ethanol (160 mL) was added to this solution, and 200 mL of NaOH solution was added to 100 g of oil and then heated at 333.15 K with magnetic stirring at 550 rpm for 1 h. After 1 h, 40 mL of water and 400 mL of hexane were added, and the solution was stirred for 1 h at room temperature. The upper layer containing unsaponifiable matter was removed and discarded. To the lower layer, 160 mL of water was added, and than 12 N hydrochloric acid (HCl) was added until the pH equaled 1. The resulting lower layer was removed by a separating funnel and discarded. The FFA-containing upper layer was dried with anhydrous Na_2SO_4 and the solvent evaporated in a vacuum rotary evaporator. The FFAs obtained by saponification of the oil were immediately analyzed. The method was modified from previous research.[25]

GC Analysis of FFA. Analyses were performed using a GC model 6890 Agilent (USA) with FID temperature set at 573.15 K and column (HP-FFAP 30 m × 0.25 mm × 0.25 μm). The oven time−temperature profile was as follows: 393.15 K (1 min), 25 K per min to 453.15 K (1 min), 5 K per min to 493.15 K (10 min), 5 K per min to 503.15 K (30 min). The carrier gas was helium with a total flow-through the column of 64.0 $mL \cdot min^{-1}$. The samples were analyzed in *n*-hexane solutions immediately after the saponification process. A quantification of FFA was made using calibration curves.

Results and Discussion

The phase behavior of the palm and coconut oils in the presence of SF_6 was studied visually by using a view cell. As can be seen from Figure 2, the system palm oil−SF_6 was composed of a lower-oil-rich phase and an upper-SF_6-rich phase in the pressure range up to 3.4 MPa at a temperature of approximately 315.15 K. The phase transition from a two- to three-phase system under these conditions for the palm oil−SF_6 system was detected due to the fact that the phase transition of SF_6 from the vapor to the liquid phase occurs at a pressure of 3.55 MPa at a temperature of 316.15 K. Another interesting feature about the palm oil−SF_6 system was noted as the pressure increased. At a temperature of 316.15 K and pressures above 3.6 MPa, the two-phase system with inversed phases (lower-SF_6-rich phase and upper-oil-rich phase) was recorded visually. This behavior is called “barotropy”,[26] and the isopynic point (point of phase inversion) was detected at 316.15 K and 3.6 MPa for the palm oil−SF_6 system.

At a higher investigated temperature of 333.15 K for the above-mentioned system, the lower phase was rich with palm oil, and the upper phase was rich with SF_6 in the areas of lower pressures up to 5.4 MPa, as can be seen from Figure 3. The isopynic point was detected at a pressure of 5.5 MPa and a temperature of 334.15 K, and at higher pressures, the two-phase system is composed of a lower-SF_6-rich phase and an upper-oil-rich phase. The three-phase equilibrium for the palm oil−SF_6 system at 333.15 K has not been detected due to the fact that at 333.15 K and at pressures above 4.1 MPa SF_6 is in the supercritical state.[27] Similar phase behavior was noted for the coconut oil−SF_6 system (Figures 4 and 5). The phase transition from a two- to three-phase system for the above-mentioned

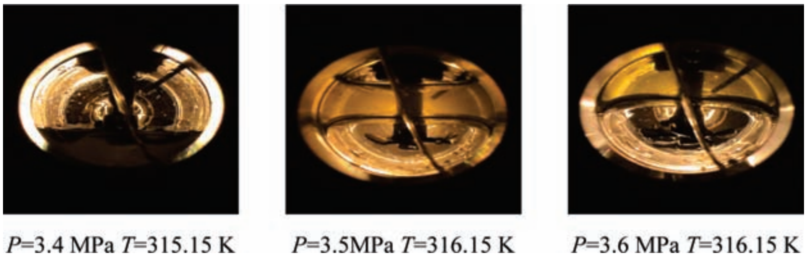
P=3.4 MPa *T*=315.15 K *P*=3.5MPa *T*=316.15 K *P*=3.6 MPa *T*=316.15 K

Figure 2. Phase equilibria for the system palm oil−sulfur hexafluoride at around 313.15 K: coexisting phases at different pressures.

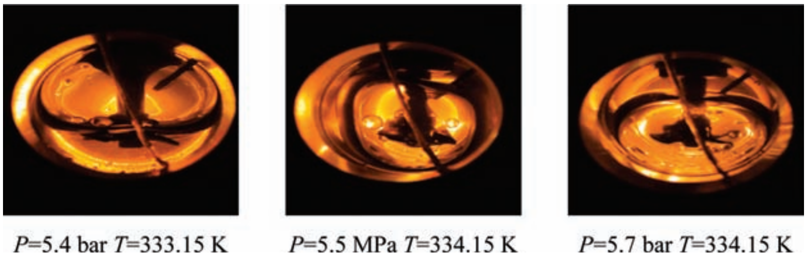
P=5.4 bar *T*=333.15 K *P*=5.5 MPa *T*=334.15 K *P*=5.7 bar *T*=334.15 K

Figure 3. Phase equilibria for the system palm oil−sulfur hexafluoride at around 333.15 K: coexisting phases at different pressures.

P=3.2 MPa *T*=312.15 K *P*=3.3 MPa *T*=314.15 K *P*=3.5MPa *T*=314.15 K

Figure 4. Phase equilibria for the system coconut oil−sulfur hexafluoride at around 313.15 K: coexisting phases at different pressures.

P=5.6 MPa *T*=333.15 K *P*=5.8MPa *T*=336.15 K *P*=5.9MPa *T*=335.15 K

Figure 5. Phase equilibria for the system coconut oil−sulfur hexafluoride at around 333.15 K: coexisting phases at different pressures.

Table 1. Equilibrium Mole Fractions of Sulfur Hexafluoride in the Upper (x_1) and Lower Phase (y_1) for the Palm Oil−Sulfur Hexafluoride System from T = (313.15 to 333.15) K

P_1/MPa	x_1	P_2/MPa	y_1
	T/K = 313.15		
0.9	0.9405 ± 0.0011	0.8	0.2132 ± 0.0001
4.9	0.1909 ± 0.0023	4.9	0.8283 ± 0.0005
8.9	0.1856 ± 0.0021	/	/
10.3	0.1856 ± 0.0022	10.9	0.8419 ± 0.0007
12.3	0.1820 ± 0.0013	/	
19	0.1819 ± 0.0015	19.5	0.8760 ± 0.0009
24.5	0.1707 ± 0.0013	/	
28.1	0.1947 ± 0.0012	29.1	0.9171 ± 0.0005
32.3	0.2051 ± 0.0009	33.3	0.9512 ± 0.0017
41.7	0.2214 ± 0.0005	41.8	0.8759 ± 0.0012
	T/K = 333.15		
1.2	0.9709 ± 0.0004	1.1	0.2082 ± 0.0006
6.9	0.2037 ± 0.0005	6.2	0.8787 ± 0.0011
10.7	0.2324 ± 0.0011	10.9	0.9186 ± 0.0012
12.9	0.2143 ± 0.0008		
14.5	0.2220 ± 0.0006	15.4	0.9659 ± 0.0011
19.1	0.2217 ± 0.0004	20.0	0.9418 ± 0.0013
24.4	0.2346 ± 0.0009	25.5	0.9801 ± 0.0009
32.6	0.2484 ± 0.0006		
36.9	0.2308 ± 0.0002	37.1	0.9580 ± 0.0007
45.5	0.2741 ± 0.0004	45.8	0.8355 ± 0.0005

system was recorded at approximately 314.15 K and 3.3 MPa, while phase inversion was recorded above 3.5 MPa, at the same temperature. At 333.15 K, the three-phase equilibria for the coconut oil−SF_6 system was not detected due to the supercritical state of SF_6 above 4.1 MPa. On the other hand, with increasing the pressure at 335.15 K, the densities of both phases changed, and phase inversion for the coconut oil−SF_6 system was detected above 5.9 MPa.

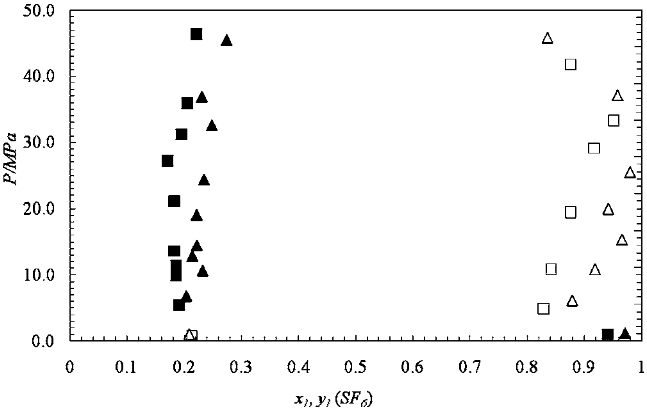

Figure 6. Phase equilibria for the system of palm oil−SF_6 at (313.15 and 333.15) K: ■, 313.15 K upper phase; □, 313.15 K lower phase; ▲, 333.15 K upper phase; Δ, 333.15 K lower phase.

In addition to phase behavior observation, the compositions of the named systems of lower and upper phases at temperatures of (313.15 and 333.15) K and in the pressure range from (1 to 50) MPa were determined. The obtained results for the palm oil−SF_6 system (Table 1, Figure 6) show that the solubility of SF_6 in palm oil increases with increasing temperature at constant pressure. On the other hand, the solubility of palm oil in SF_6 decreases with increasing temperature at constant pressure and decreases with increasing pressure up to 32 MPa, at constant temperature (Figure 6). As can be seen from Figure 6, the solubility of palm oil in SF_6 at 313.15 K is in the range from (0.05 to 0.17) mol fractions, while at 333.15 K it is between (0.02 and 0.16) mol fractions. On the contrary, solubility of palm oil in CO_2 is between (0.00014 and 0.0025) mol fraction at the same temperatures and pressures.[15,18] It can be concluded that the solubility of palm oil in CO_2 is more than 100 times lower than in SF_6 under the same high-pressure conditions.

Solubility data for the coconut oil−SF_6 system are presented in Figure 7 and Table 2. The obtained results show that the solubility of SF_6 in coconut oil increases with increasing temperature at constant pressure. However, the composition of the SF_6-rich phase is not significantly changed with increasing temperature and pressure. The solubility of coconut oil in SF_6 is somewhat lower than that of palm oil and is around 0.06 mol fraction at both investigated temperatures.

In our previous research,[23] it was observed that the solubility of SF_6 in sunflower and soyabean oils generally decreases with increasing temperature. On the other hand, our present research shows that the solubility of SF_6 in the above-mentioned oils generally increases with increasing temperature. Therefore, it can be concluded that the solubility of SF_6 in vegetable oils depends on their chemical composition, especially on saturated and unsaturated fatty acid (FA) content. In present research, the fatty acid contents of palm, coconut, soyabean, and sunflower oils have been determined by GC analyses, and the results are presented in Table 3. Additionally, the mass fraction ratio between saturated and unsaturated fatty acids has been calculated and is shown in Table 4.

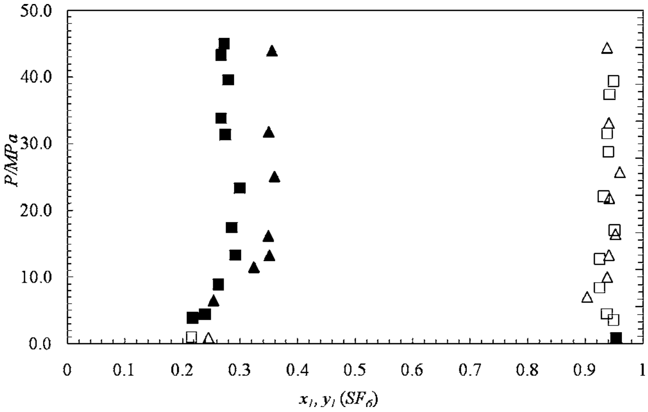

Figure 7. Phase equilibria for the system of coconut oil−SF_6 at (313.15 and 333.15) K: ■, 313.15 K upper phase; □, 313.15 K lower phase; ▲, 333.15 K upper phase; Δ, 333.15 K lower phase.

Table 2. Equilibrium Mole Fractions of Sulfur Hexafluoride in the Upper (x_1) and Lower (y_1) Phase for the Coconut Oil−Sulfur Hexafluoride System from T = (313.15 to 333.15) K

P_1/MPa	x_1	P_2/MPa	y_1
	T/K = 313.15		
0.8	0.9533 ± 0.0001	1.0	0.2154 ± 0.0006
3.5	0.2173 ± 0.0009	3.6	0.9488 ± 0.0011
4.0	0.2389 ± 0.0011	4.5	0.9369 ± 0.0012
8.0	0.2624 ± 0.0013	8.4	0.9252 ± 0.0008
12.0	0.2921 ± 0.0006	12.7	0.9250 ± 0.0012
15.7	0.2859 ± 0.0007	17.1	0.9511 ± 0.0009
21.0	0.2993 ± 0.0008	22.1	0.9320 ± 0.0004
28.2	0.2745 ± 0.0005	28.8	0.9401 ± 0.0006
30.4	0.2670 ± 0.0004	31.5	0.9376 ± 0.0011
/	/	37.4	0.9422 ± 0.0005
35.6	0.2789 ± 0.0007	/	/
39	0.2675 ± 0.0009	39.4	0.9488 ± 0.0007
40.5	0.2725 ± 0.0012	/	/
	T/K = 333.15		
0.8	0.9543 ± 0.0005	0.9	0.2456 ± 0.0006
6.5	0.2543 ± 0.0007	7.0	0.9033 ± 0.0008
11.5	0.3244 ± 0.0005	10.0	0.9382 ± 0.0012
13.3	0.3513 ± 0.0006	13.3	0.9412 ± 0.0009
16.2	0.3493 ± 0.0009	16.5	0.9525 ± 0.0007
/	/	21.8	0.9420 ± 0.0007
25.1	0.3601 ± 0.0004	25.7	0.9601 ± 0.0004
31.8	0.3501 ± 0.0009	33.1	0.9411 ± 0.0008
44.0	0.3558 ± 0.0006	44.4	0.9381 ± 0.0011

Table 3. Chemical Composition of Vegetable Oils (Palm Oil, Coconut Oil, Sunflower Oil, and Soyabean Oil) in Mass Fractions

compound (FFA)	palm oil	coconut oil	sunflower oil	soyabean oil
dodecanoic acid	0.033	0.451	/	/
tetradecanoic acid	0.043	0.146	/	/
hexanoic acid	/	0.007	/	/
octanoic acid	/	0.085	/	/
decanoic acid	/	0.064	/	/
hexadecanoic acid	0.356	0.068	0.089	0.159
(9*Z*)-octadec-9-enoic acid	0.376	0.088	0.307	0.316
octadecanoic acid	0.044	0.017	0.036	0.045
cis,*cis*,9,12-octadecadienoic acid	0.148	0.074	0.568	0.432
(9*Z*,12*Z*)-octadeca-9,12-dienoic acid	/	/	/	0.043

When comparing both vegetable oil−SF_6 systems at a lower investigated temperature of 313.15 K (Figure 8), it was found that SF_6 shows better solubility in coconut oil than in palm oil, while the solubility of palm oil in SF_6 is higher than the solubility of coconut oil. Similar conclusions can be done also for solubility results at 333.15 K (Figure 9). Therefore, the solubility of vegetable oils in SF_6 is higher for oils with a higher content of unsaturated fatty acids.

Table 4. Mass Fraction Ratio (w) between Saturated and Unsaturated Fatty Acids in Vegetable Oils

vegetable oil	w
palm oil	0.476/0.524
coconut oil	0.838/0.162
sunflower oil	0.125/0.875
soyabean oil	0.219/0.791

Figure 10 shows a comparison between the phase equilibrium solubility data obtained for different vegetable oils (sunflower, palm, soyabean and coconut oils) in SF_6 at 313.15 K. The obtained results show that SF_6 is the most soluble in coconut oil, while it is less soluble in palm and soyabean oils. The lowest solubility of SF_6 is in sunflower oil. The obtained results can be explained based on the fact that solubility is influenced by the FA compositions of vegetable oils.

The solubility of SF_6 in oil increases with increasing temperature if the content of saturated acids in vegetable oils (palm and coconut oils) is higher than or similar to the contents of unsaturated acids. On the other hand, the molar fraction of SF_6 in oil decreases with increasing temperature at constant pressure, if the vegetable oil is rich with unsaturated fatty acids (sunflower and soyabean oils).

Conclusion

In the presented research, the phase equilibria for the palm oil−SF_6 and coconut oil−SF_6 systems were investigated at two

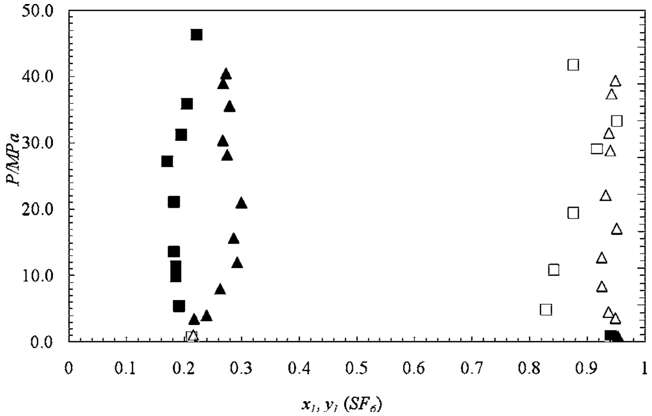

Figure 8. Phase equilibria for vegetable oil−SF_6 systems at 313.15 K. Comparison of experimental data: ■, 313.15 K upper phase palm oil; □, 313.15 K lower phase palm oil; ▲, 313.15 K upper phase coconut oil; Δ, 313.15 K lower phase coconut oil.

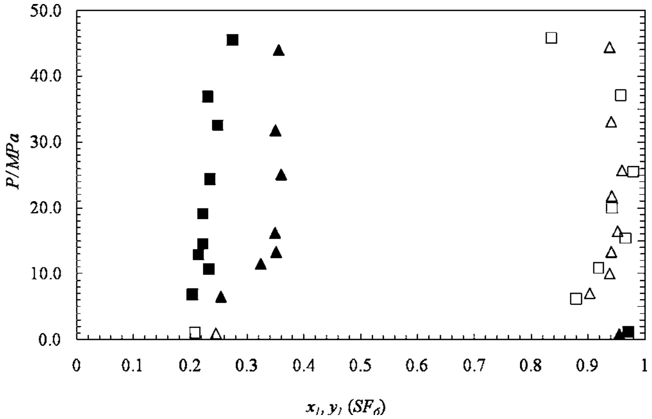

Figure 9. Phase equilibria for vegetable oil−SF_6 systems at 333.15 K. Comparison of experimental data: ■, 333.15 K upper phase palm oil; □, 333.15 K lower phase palm oil; ▲, 333.15 K upper phase coconut oil; Δ, 333.15 K lower phase coconut oil.

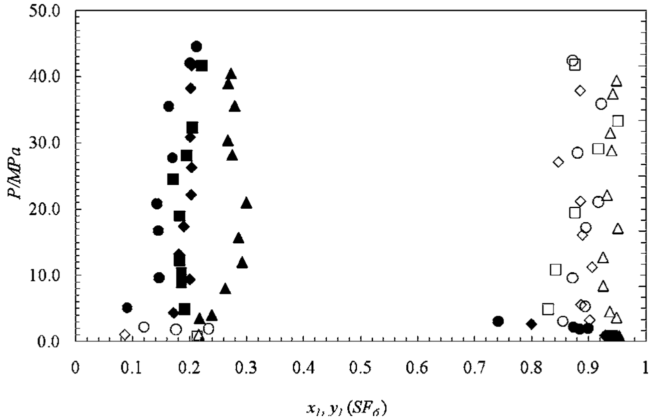

Figure 10. Phase equilibria for systems of vegetable oil−SF_6 at 313.15 K: comparison of experimental and literature data: ■, 313.15 K upper phase palm oil; □, 313.15 K lower phase palm oil; ▲, 313.15 K upper phase coconut oil; Δ, 313.15 K lower phase coconut oil; ♦, 313.15 K upper phase soyabean oil, ref 23; ◊, 313.15 K lower phase soyabean oil, ref 23; ●, 313.15 K upper phase sunflower oil, ref 23; ○, 313.15 K lower phase sunflower oil, ref 23.

different temperatures. For both the above-mentioned systems, at a temperature of 313.15 K, a three-phase system was obtained at a pressure of around 3.5 MPa, while at 333.15 K, the transition from a two- to a three-phase system was not observed. This behavior can be explained by the phase transition of SF_6 from a vapor to a liquid state at 313.15 K and 3.325 MPa, while at 333.15 K the SF_6 is in the vapor state below 3.8 MPa and in the SCF state above this pressure.

Generally, the isopynic point was noted at around 313.2 K at approximately above 3.5 MPa, while at 333.15 K phase inversion was noted at approximately 5.5 MPa. The solubility of SF_6 in vegetable oils was up to 0.2741 mol fraction for palm oil and up to 0.3622 mol fraction for coconut oil. The solubility of SF_6 in oil generally increases with increasing temperature and with the mass percent of saturated fatty acids in vegetable oils. The solubility for both vegetable oils in SF_6 under the investigated conditions is generally between (0.02 and 0.17) mol fractions which is more than 100 times higher than in CO_2.

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