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High-Pressure *PVT* Behavior of Natural Fats and Oils, Trilaurin, Triolein, and *n*-Tridecane from 303 K to 353 K from Atmospheric Pressure to 150 MPa

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High-pressure *PVT* data are lacking for many natural oil systems that are processed with supercritical fluids. In this work, we report on the *PVT* behavior of beef shank, beef tallow, coconut, palm, and palm kernel fats and castor, menhaden, linseed, olive, perilla, safflower, sesame, and soybean oils, each of which was characterized by a fatty acid distribution, iodine value, and saponification value. In addition, we report on the *PVT* behavior of pure components trilaurin, triolein, and tridecane. Well over 800 *PVT* data were measured with a static-type bellows apparatus. *PVT* behavior of the fats showed a marked change in crystallinity with increasing temperature and pressure. *PVT* behavior for the fats and oils above their melting point was similar, as expected, but could be explained in terms of molecular weight, iodine value, and to some extent, fatty acid composition. At a given temperature and pressure, the specific volume of the oils decreased with increasing iodine value. The data were correlated with the Tait, Peng−Robinson, Hederer−Peter−Wenzel, lattice, Flory, and simplified perturbed hard chain theory (SPHCT). As expected from their functional form, all cubic equations performed poorly in the compressed liquid region. Only the Tait, Flory, and SPHCT equations provided satisfactory correlation. SPHCT parameters were determined for all fats and oils. These parameters were generalized in terms of measurable oil properties, saponification value, and iodine value. The parameter, "*c*", which is related to the number of degrees of freedom, was found to be slightly temperature dependent. With the correlated parameters, *PVT* behavior of the oils could be described to within 4.9% average error in pressure.

Introduction

Properties such as density, compressibility, expansivity, and phase transitions are important in the design of extraction and reaction unit operations. We recently reported on supercritical fluid extraction of fats and oils from collagen−fat mixtures with carbon dioxide + propane mixtures (Acosta et al., 1995) and found that pressure had a great effect on solubility. Many other researchers have studied the extraction of oils and fats with dense gases such as carbon dioxide or other fluids. Typical extraction and solubility measurements of fats and oils include those of Stahl et al. (1988), King et al. (1989), Tilly et al. (1990), and Bharath et al. (1992). Other authors (Bamberger et al., 1988; Ohgaki et al., 1989; Ashour and Hammam, 1993) have made solubility measurements of glyceride components to provide information on model component phase behavior. However, despite these studies, the pressure dependence of the physical properties for fats and oils is virtually unknown. The objective of this work is to provide a comprehensive set of pressure−volume−temperature data for fats and oils that have been characterized and to correlate the data with suitable equations.

Material and Methods

Mercury and tridecane were obtained from Wako Chemicals (Osaka, Japan) and were of 99.99% and 99% minimum purity, respectively. Triolein and trilaurin were obtained from Sigma Chemicals (St. Louis, MO) and were of 99% minimum purity. Table 1 gives the source, the saponification number, iodine value, and fatty acid distribution of the fats and oils used. The saponification number and iodine values were determined by JOCS (Japan Oil Chemists' Society) methods 2.4.3.1−71 and 2.4.5.1−71, respectively. The fatty acid distribution was determined by using gas chromatography after methanolysis by JOCS method 2.4.20.2−77. The molecular weights were calculated as discussed in the next section.

Tridecane was used to check the adequate functioning of the experimental apparatus and to verify the experimental procedure. The fats and oils were chosen such that a wide range of properties was obtained. The iodine value ranged from 9.7 for coconut oil to 187.8 for linseed oil. The saponification value ranged from 180.9 for castor oil to 257 for coconut oil. The beef shank fat is that reported by Acosta et al. (1995).

The *PVT* behavior was measured using a commercially available computer-controlled *PVT* apparatus (GNOMIX, Boulder, CO) which could measure specific volumes from 10 MPa to 200 MPa. The apparatus, which is based on a confining fluid and a flexible bellows technique, is described in more detail by Fakhreddine and Zoller (1994). Mercury, the confining fluid, and 1 to 2 g of the sample were contained in a sample cell that was closed off at one end by a flexible bellows. The sample cell was placed in a high-pressure vessel, and a hydrostatic pressure of silicon oil was applied to the sample cell with a high-pressure pump. The combined expansion or compression of the confining fluid and sample was measured with a linear variable differential transducer (LVDT) attached to the bellows. The resolution of the LVDT was 0.001 mm, which represented a specific volume change of 0.0001 $cm^3 \cdot g^{-1}$.

The temperature was measured with a K-type thermocouple, to a resolution of 0.1 K, that touched the cell directly. The thermocouple was calibrated against a secondary standard platinum resistance thermometer that was NIST traceable and accurate to 0.01 K. Pressure was

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Table 1. Properties and Sources for Fats and Oils

				fatty acid distribution (g/100 g of total fatty acids)[d]												
fat/oil	MW[a]	IV[b]	SV[c]	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	$C_{16:1}$	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	other	source[e]
beef shank	788.7	45.3	213.4					3.4	28.2	3.5	15.9	39.3	0.3			A
beef tallow	857.9	48.2	196.2					2.7	25.7	2.9	17.2	41.3	2.9			B
coconut	654.9	9.7	257.0	0.5	7.1	6.0	47.8	18.2	9.0		2.6	6.7	1.9			C
palm	691.2	18.6	243.5		1.0	2.9	48.3	16.6	8.7		2.1	17.0	2.9			D
palm kernel	647.4	18.0	260.0			3.3	46.7	16.2	9.0		2.2	16.8	2.5		0.1 C_{20}	D
castor	930.4	84.8	180.9						2.0		2.2	6.7	8.9		75.9 ricinoleic	B
fish (menhaden)	870.7	179.4	193.3					8.9	15.6	11.6	2.7	7.3	1.3	1.1	3.3 ($C_{18:4}$) 0.7 ($C_{20:4\omega6}$) 1.7 ($C_{20:4\omega3}$) 14.0 ($C_{20:5}$) 2.2 ($C_{22:5}$) 10.6 ($C_{22:6}$)	C
linseed	876.6	187.8	192.0						5.8		3.5	20.4	15.1	51.7		B
olive	882.1	73.7	190.8						10.3	0.9	4.1	79.3	3.8	0.6		B
perilla	870.3	186.8	193.4						6.4	0.1	2.3	20.1	13.3	56.1		B
safflower	875.3	144.2	192.3						6.6	0.1	2.5	12.4	76.3	0.1		C
sesame	887.7	109.2	189.6						9.3	0.2	6.2	41.7	41.0	0.3		B
soybean	877.5	132.5	191.8						10.6	0.1	4.0	23.6	52.0	5.7		B

[a] MW: molecular weight calculated from SV. See text. [b] IV: iodine value [c] SV: saponification value [d] C_8, caprylic; C_{10}, capric; C_{12}, lauric; C_{14}, myristic; C_{16}, palmitic; C_{18}, stearic; $C_{18:1}$, oleic; $C_{18:2}$, linoleic; $C_{18:3}$, linolenic. [e] A: Teepak, Inc. (Sandy Run, SC) and Acosta et al. (1995). B: Wako Pure Chemical Industries (Osaka, Japan). C: Sigma Chemical (St. Louis, MO). D: NOF Corp. (Tsukuba, Japan).

measured with a gauge that was accurate to 0.1%. During a run, temperature and pressure would slowly drift but never exceeded 0.5 K and 0.1 MPa, respectively. However, the precise temperature and pressure of each measurement were always recorded by computer and are given in the tables discussed below.

The sample cell was first loaded with mercury using a vacuum filler assembly described in Zoller (1976). A known mass of mercury was removed and replaced by 1 to 2 g of liquid sample. The sample cell was then attached to the apparatus, and measurements were performed. For fats, these were gently melted and loaded as liquids in the cell. The loading of the mercury and sample was determined by mass difference to within 0.1 mg. The substances were checked for compatibility with mercury by visual inspection before and after each run, by replicate runs, and by contacting the samples with mercury at room temperature during the year long experiments. No reaction or visible change was noted. Further details are given in Acosta (1995).

The *PVT* behavior of the fats and oils was measured using the isothermal mode of operation. The system was first stabilized after the cell was initially loaded. Following this, the system was stabilized at a given temperature and 10 MPa for 15 min. Pressure was then increased, allowing 10 to 15 min stabilization time after each pressure increment.

All the oils and fats were measured at (303, 313, 333, and 353) K, at pressures between (10 and 145) MPa in increments of 15 MPa. For the fats, additional measurements were performed at temperatures between (294 and 303) K. Three replicates were performed with tridecane and sesame oil. Two replicates were made with coconut, linseed, and soybean oils. All other oils and fats had only one replicate. Each replicate consisted of a different sample of the substance and measurement at the same conditions.

The atmospheric densities of each oil and fat shown in Table 2 were measured with a 10 mL pycnometer in a water bath that had been calibrated with distilled degassed water. Temperatures were chosen such that the substances were in the liquid state. These data provide reference values for the apparatus and correlation equations discussed later. The procedure was checked by measuring the density of tridecane and comparing with literature values (Vargaftik, 1975). The water calibration was performed with five replicates. The tridecane, oil, and fat densities were measured with three replicates.

Table 2. Atmospheric Densities of Oils and Fats

substance	T/K	ρ/g·cm^{-3}
trilaurin	333.2	0.8925
triolein	303.2	0.9044
beef shank	323.2	0.8965
beef tallow	323.2	0.8902
coconut	303.2	0.9122
palm	303.2	0.9124
palm kernel	303.2	0.8874
castor oil	303.2	0.9532
fish oil	303.2	0.9224
linseed oil	303.2	0.9222
olive oil	303.2	0.9050
perilla oil	303.2	0.9220
safflower oil	303.2	0.9161
sesame oil	303.2	0.9124
soybean oil	303.2	0.9130

Results

Pure component *PVT* behavior is discussed first. Table 3 shows the *PVT* behavior measured for tridecane compared with literature data (Vargaftik, 1975) that was adjusted to our measured experimental conditions with 2-dimensional cubic interpolation (Krogh, 1970). Our data agreed with the literature values to within 0.10% with the largest deviation in specific volume being 0.0024 cm^3/g. This confirmed the procedure and measurement technique.

The values at 0.1 MPa were obtained by extrapolating high-pressure values to atmospheric values with the procedure developed by Zoller et al. (1976). The procedure uses the difference between polynomials fit to the sample volume changes and polynomials fit to the mercury volume changes in addition to the temperature and pressure characteristics of the bellows. Because the properties of mercury are well-known and a density difference is used, the procedure has been shown to be reliable (Zoller et al., 1976). From the table, it can be seen that the procedure also provides reliable extrapolated volumes over the range of temperatures in this work. This procedure was also used for the oil data at 0.1 MPa.

Figure 1 and Table 4 show the *PVT* for trilaurin, a C_{12} monoacid triglyceride that is solid at room temperature. The $V-T$ plot is a cross-plot of the $P-V$ data since all experiments were run in isothermal mode. The β-crystalline form has a melting point of 319.6 K (Ollivon and

Table 3. *PVT* for Tridecane and Comparison with Literature Values of Vargaftik (1975)

T/K	P/MPA	V^{exp}/ cm^3·g^{-1}	V^{lit}/ cm^3·g^{-1}	$\Delta V = V^{exp} - V^{lit}$/cm^3·g^{-1}	$100\Delta V/V^{lit}$
303.0	0.1	1.3351[a]	1.3346	0.00049	0.0366
303.5	9.0	1.3232	1.3235	−0.00031	−0.0237
303.9	19.0	1.3123	1.3124	−0.00012	−0.0094
303.9	29.0	1.3024	1.3020	0.00042	0.0323
303.9	39.0	1.2933	1.2924	0.00087	0.0674
303.9	49.0	1.2849	1.2837	0.00124	0.0968
303.9	69.0	1.2700	1.2678	0.00215	0.1699
303.9	89.0	1.2563	1.2541	0.00223	0.1779
303.8	99.0	1.2499	1.2477	0.00217	0.1741
303.8	109.0	1.2441	1.2418	0.00229	0.1843
303.8	129.0	1.2330	1.2308	0.00221	0.1798
303.7	149.0	1.2228	1.2204	0.00240	0.1968
323.3	0.1	1.3585[a]	1.3609	−0.00240	−0.1763
322.8	9.0	1.3450	1.3468	−0.00184	−0.1365
322.9	19.0	1.3327	1.3339	−0.00124	−0.0927
322.9	29.0	1.3217	1.3222	−0.00054	−0.0407
322.9	39.0	1.3116	1.3116	−0.00003	−0.0026
323.0	49.0	1.3024	1.3021	0.00033	0.0250
323.0	69.0	1.2862	1.2847	0.00145	0.1130
323.0	89.0	1.2716	1.2698	0.00181	0.1428
324.1	99.0	1.2655	1.2639	0.00160	0.1263
324.1	109.0	1.2585	1.2575	0.00098	0.0777
324.1	129.0	1.2466	1.2457	0.00090	0.0722
324.1	149.0	1.2358	1.2347	0.00111	0.0900

AAPD[b] = 0.1019 BIAS[b] = 0.0008

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation. [b] AAPD = $1/N\sum|V^{exp} - V^{lit}|/V^{lit}100\%$. BIAS = $1/N\sum(V^{exp} - V^{lit})100\%$.

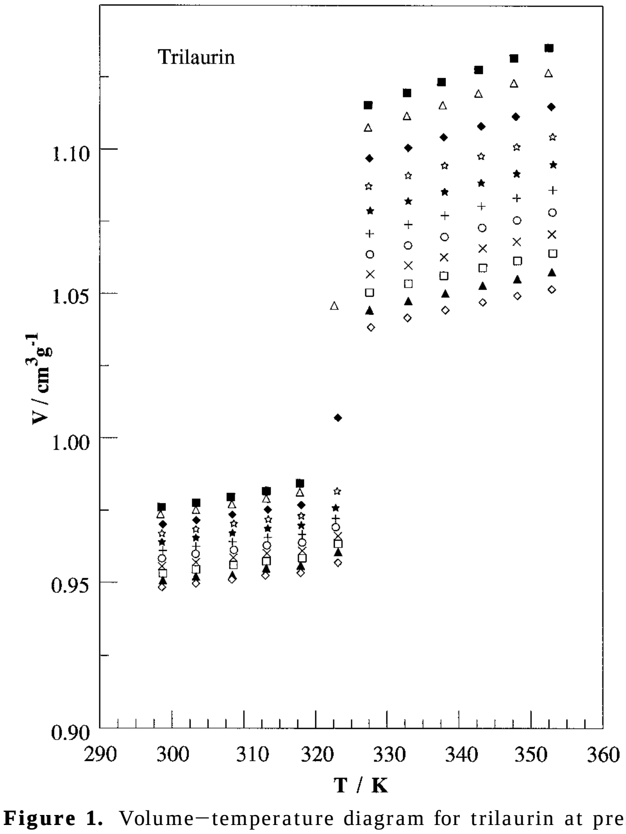

Figure 1. Volume−temperature diagram for trilaurin at pressures up to 99 MPa. Pressures in MPa: 0.1 (filled squares); 9.0 (triangles); 24.0 (filled diamonds); 39.0 (stars); 54.0 (filled stars); 69.0 (crosses); 84.0 (circles); 99.0 (x-marks); 114.0 (squares); 129.0 (filled triangles); 144 (diamonds).

Perron, 1982). As shown by the figure, the melting point is relatively sharp, which is expected since trilaurin is a pure substance. The melting point is not as sharp as that of normal crystalline solids because the triglycerides generally exist as polymorphic solids with an unstable α-phase, a less stable β'-phase, and a stable β-phase. The subject of equilibrium between polymorphic states has been studied by Wesdorp (1990). Although it is not the subject of this study, the reported changes in crystallinity of all solid phase data may be interpreted in terms of the equilibria between the α, β, and β' phases. Figure 2 shows the *PVT* behavior for beef shank fat, which has a fatty acid composition that is very close to that of beef tallow fat. As for all of the fats measured, the change in specific volume was gradual and did not exhibit a sharp break in volume like that found for trilaurin. The crystallinity gradually changed with temperature and pressure, as it did for the other fats. The pressure dependence on the melting point can be seen from the change in slope of the $V-T$ solid phase lines as pressure increases.

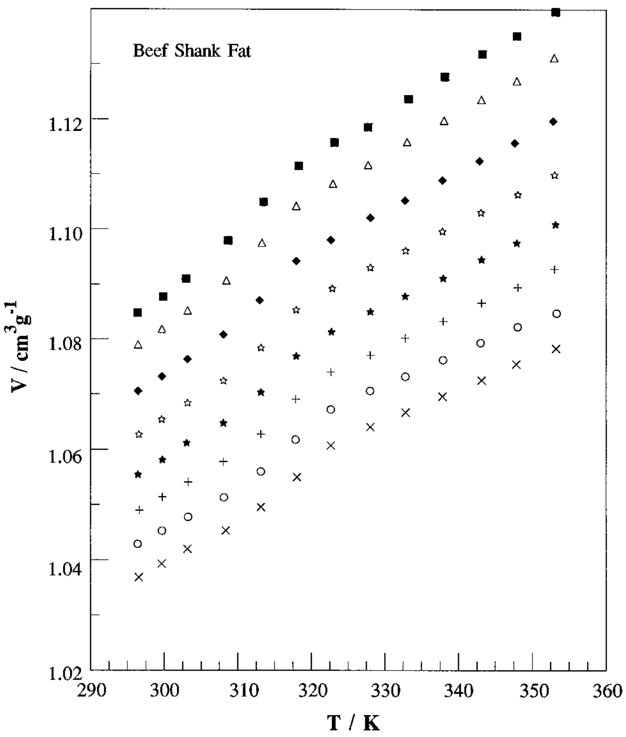

Figure 2. Volume−temperature diagram for beef shank fat at pressures up to 99 MPa showing the gradual change in fat crystallinity. Pressures in MPa: 0.1 (filled squares); 9.0 (triangles); 24.0 (filled diamonds); 39.0 (stars); 54.0 (filled stars); 69.0 (crosses); 84.0 (circles); 99.0 (x-marks).

The molecular weights of the the oils and fats were calculated from the saponification value according to the correlation given by Swern (1979) are shown in Table 1. It is also possible to calculate the molecular weight from the fatty acid distribution, as suggested by Halvorsen et al. (1993). We compared the values from the two different methods and found them generally to agree with each other to within 1% or less. Exceptions were for palm kernel, beef shank, and castor in which the molecular weights determined by the two methods differed by 9.1%, 7.8%, and 2.4%, respectively. These differences can be attributed to the less refined nature of the beef shank fat and palm kernel oil and other factors such as chromatography calibration and fatty acid normalization.

Figure 3 contains a summary of the *PVT* behavior of oils at 333 K. From the figure, it is apparent that all oils in the liquid state are isotropic and do not show any type of phase transition over the range of conditions measured. There are at least three primary factors that influence the grouping of the oil and fat curves on the diagram. The first factor is molecular weight. Palm kernel oil, which has the lowest molecular weight, and castor oil, which has the highest molecular weight, expand the most and the least,

Table 4. *PVT* for Trilaurin

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
298.5	9	0.9737	303.4	9	0.9752	308.4	9	0.9772	313.2	9	0.9792
298.8	24	0.9702	303.5	24	0.9716	308.5	24	0.9735	313.4	24	0.9753
298.7	39	0.9669	303.4	39	0.9684	308.7	39	0.9704	313.5	39	0.9719
298.7	54	0.9639	303.4	54	0.9654	308.5	54	0.9671	313.4	54	0.9687
298.8	69	0.9610	303.4	69	0.9625	308.5	69	0.9641	313.4	69	0.9656
298.7	84	0.9582	303.4	84	0.9597	308.5	84	0.9612	313.3	84	0.9628
298.7	99	0.9556	303.4	99	0.9570	308.7	99	0.9586	313.3	99	0.9600
298.8	114	0.9531	303.4	114	0.9545	308.6	114	0.9560	313.2	114	0.9574
298.8	129	0.9507	303.4	129	0.9520	308.5	129	0.9526	313.2	129	0.9549
298.7	144	0.9483	303.4	144	0.9496	308.4	144	0.9510	313.1	144	0.9524
						327.4	0.1	1.1154[a]	332.8	0.1	1.1197[a]
317.9	9	0.9814	322.7	9	1.0459	327.4	9	1.1076	332.8	9	1.1117
318.1	24	0.9769	323.2	24	1.0070	327.6	24	1.0969	333.0	24	1.1006
318.1	39	0.9731	323.1	39	0.9817	327.5	39	1.0873	333.0	39	1.0909
318.1	54	0.9698	322.9	54	0.9759	327.7	54	1.0787	333.0	54	1.0821
318.2	69	0.9667	322.9	69	0.9723	327.6	69	1.0709	333.0	69	1.0741
318.2	84	0.9638	322.9	84	0.9692	327.7	84	1.0636	333.0	84	1.0667
318.2	99	0.9609	323.2	99	0.9661	327.7	99	1.0568	333.0	99	1.0599
318.2	114	0.9584	323.2	114	0.9634	327.6	114	1.0505	333.0	114	1.0535
318.0	129	0.9558	323.2	129	0.9605	327.6	129	1.0443	333.0	129	1.0475
318.0	144	0.9533	323.2	144	0.9569	327.8	144	1.0384	332.9	144	1.0417
337.6	0.1	1.1235[a]	342.8	0.1	1.1278[a]	347.7	0.1	1.1317[a]	352.6	0.1	1.1355[a]
337.8	9	1.1155	342.8	9	1.1195	347.7	9	1.1232	352.5	9	1.1268
338.0	24	1.1042	343.2	24	1.1081	348.0	24	1.1115	352.9	24	1.1150
338.1	39	1.0944	343.2	39	1.0977	348.1	39	1.1010	353.1	39	1.1044
338.1	54	1.0854	343.2	54	1.0885	348.1	54	1.0916	353.2	54	1.0948
338.1	69	1.0773	343.2	69	1.0804	348.1	69	1.0833	353.1	69	1.0861
338.1	84	1.0697	343.3	84	1.0729	348.2	84	1.0755	353.1	84	1.0782
338.0	99	1.0628	343.4	99	1.0658	348.1	99	1.0682	353.0	99	1.0708
338.0	114	1.0563	343.4	114	1.0591	348.2	114	1.0616	353.1	114	1.0642
338.2	129	1.0502	343.4	129	1.0529	348.2	129	1.0552	353.0	129	1.0576
338.2	144	1.0444	343.4	144	1.0471	348.2	144	1.0494	353.0	144	1.0516

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

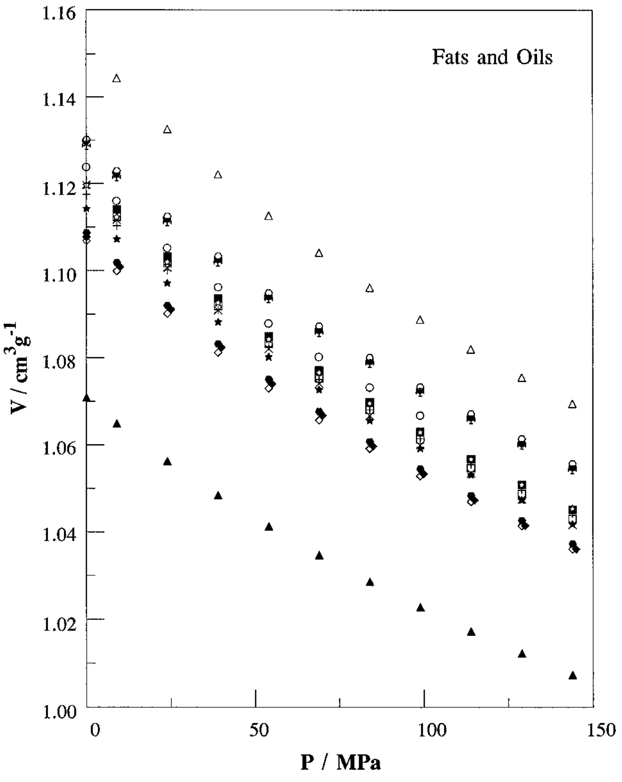

Figure 3. *PVT* of fats and oils at 333 K. Substances: beef shank (circles); beef tallow (filled circles); coconut (squares); palm (filled squares); palm kernel (triangles); castor (filled triangles); menhaden fish (diamonds); linseed (filled diamonds); olive (hexagons); perilla (filled hexagons); safflower (filled stars); sesame (stars); soybean (crosses); triolein (capped crosses); trilaurin (x-marks).

respectively. The second factor is fatty acid distribution and structure. Castor oil had the lowest specific volume and expanded the least with pressure. The *PVT* behavior of castor oil was very distinguishable from the other oils, which can be attributed to the hydroxylated fatty acid chain of the triglyceride. Olive oil had a specific volume that was comparable with that of triolein. Sesame and soybean oil had similar *PVT* behavior. Perilla and linseed oil behaved similarly. Substances with similar molecular weights and similar fatty acid distributions tended to exhibit similar *PVT* behavior. The third factor is the iodine value. When the fatty acid composition of the oil is examined, olive and triolein are high in oleic acid. Sesame and soybean oils are high in oleic and linoleic acids; safflower is high in linolenic acid. Perilla and linseed oils are rich in oleic and linolenic acids, and fish oil contains a high percentage of highly C_{20} unsaturated acids. Except for castor oil, at a given pressure, the specific volumes of the oils were proportional to the iodine number, with the specific volume decreasing with increasing iodine value. Those with high iodine values expanded more than those with lower values. A fourth factor, which was not examined in this work, is the distribution of the fatty acids on the glyceryl subunit that can affect packing and packing volumes.

Tables 2–18 contain approximately 800 *PVT* data for all the substances studied in this work. The extrapolated specific volumes, as discussed previously, were within 0.05% of the values of those oils measured with the pycnometer at 303 K.

Data Correlation

The liquid specific volumes were correlated with the Tait equation and equations of state. The form of the Tait equation used was

$$v = v_0[1 + c \log_e((P + B)/(P_0 + B))] \qquad (1)$$

where "c" is a constant, $B(T)$ is a temperature dependent constant, and v_0 and P_0 are a reference volume and pressure at a known condition. Reference values for v_0 and P_0 are given in Table 2. The Tait equation could fit the data to within 1.6% in pressure except for beef shank fat

Table 5. *PVT* for Triolein

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.1059[a]	312.7	0.1	1.1132[a]	332.6	0.1	1.1287[a]	352.2	0.1	1.1447[a]
303.1	9	1.0995	312.8	9	1.1066	332.6	9	1.1215	352.2	9	1.1365
303.1	24	1.0904	312.8	24	1.0971	332.8	24	1.1111	352.4	24	1.1251
303.1	39	1.0822	312.7	39	1.0886	332.8	39	1.1019	352.4	39	1.1151
303.1	54	1.0746	312.7	54	1.0807	332.8	54	1.0935	352.6	54	1.1062
303.1	69	1.0676	312.7	69	1.0737	332.8	69	1.0858	352.7	69	1.0979
303.1	84	1.0612	312.8	84	1.0668	332.7	84	1.0787	352.7	84	1.0903
303.1	99	1.0552	312.8	99	1.0606	332.7	99	1.0721	352.7	99	1.0832
303.3	114	1.0494	312.8	114	1.0547	332.7	114	1.0658	352.7	114	1.0768
303.1	129	1.0439	312.8	129	1.0491	332.8	129	1.0599	352.7	129	1.0705
303.1	144	1.0389	312.8	144	1.0440	332.8	144	1.0543	352.7	144	1.0646

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 6. *PVT* for Beef Shank Fat

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
296.5	9	1.0790	298.7	9	1.0818	303.1	9	1.0852	308.5	9	1.0907
296.5	24	1.0705	299.7	24	1.0732	303.1	24	1.0763	308.1	24	1.0808
296.6	39	1.0627	299.7	39	1.0654	303.1	39	1.0684	308.1	39	1.0724
296.5	54	1.0554	299.8	54	1.0581	303.1	54	1.0612	308.1	54	1.0648
296.7	69	1.0490	299.8	69	1.0514	303.3	69	1.0541	308.1	69	1.0578
296.5	84	1.0428	299.8	84	1.0452	303.3	84	1.0477	308.2	84	1.0513
296.6	99	1.0369	299.7	99	1.0393	303.1	99	1.0420	308.4	99	1.0453
296.6	114	1.0314	299.7	114	1.0336	303.1	114	1.0365	308.2	114	1.0397
296.9	129	1.0255	299.8	129	1.0283	303.1	129	1.0313	308.3	129	1.0343
297.0	144	1.0191	299.7	144	1.0228	303.3	144	1.0261	308.2	144	1.0291
313.3	9	1.0975	318.0	9	1.1042	323.0	9	1.1083	328.2	9	1.1117
313.0	24	1.0871	318.0	24	1.0942	322.7	24	1.0980	328.5	24	1.1021
313.2	39	1.0784	318.0	39	1.0853	322.9	39	1.0892	328.5	39	1.0930
313.2	54	1.0703	318.0	54	1.0769	322.8	54	1.0813	328.5	54	1.0850
313.2	69	1.0628	317.9	69	1.0691	322.7	69	1.0740	328.5	69	1.0771
313.2	84	1.0560	317.9	84	1.0618	322.7	84	1.0672	328.5	84	1.0705
313.2	99	1.0496	318.1	99	1.0550	322.7	99	1.0608	328.5	99	1.0641
312.8	114	1.0434	318.0	114	1.0481	322.6	114	1.0557			
312.9	129	1.0378	318.0	129	1.0421	322.7	129	1.0497			
313.0	144	1.0325	317.1	144	1.0366	322.7	144	1.0428			
333.1	9	1.1159	343.2	9	1.1236	353.0	9	1.1312			
332.8	24	1.1052	342.9	24	1.1124	352.9	24	1.1197			
332.9	39	1.0961	343.1	39	1.1030	353.1	39	1.1099			
332.8	54	1.0878	343.2	54	1.0945	353.2	54	1.1009			
332.9	69	1.0802	343.2	69	1.0866	353.1	69	1.0928			
332.9	84	1.0732	343.1	84	1.0793	353.4	84	1.0847			
332.9	99	1.0667	343.2	99	1.0725	353.3	99	1.0754			
332.6	114	1.0614									
332.7	129	1.0556									
332.7	144	1.0657									

Table 7. *PVT* for Beef Tallow Fat

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
302.9	9	1.0853	312.4	9	1.0975	317.5	9	1.1061	322.4	9	1.1158
302.8	24	1.0764	312.6	24	1.0871	317.8	24	1.0944	322.4	24	1.1051
303.0	39	1.0682	312.6	39	1.0779	317.7	39	1.0843	322.4	39	1.0949
302.9	54	1.0605	312.6	54	1.0697	317.7	54	1.0753	322.4	54	1.0849
303.0	69	1.0533	312.6	69	1.0620	317.6	69	1.0674	322.5	69	1.0747
303.0	84	1.0466	312.7	84	1.0549	317.6	84	1.0600	322.4	84	1.0655
302.9	99	1.0403	312.6	99	1.0482	317.6	99	1.0533	322.5	99	1.0578
303.0	114	1.0344	312.8	114	1.0419	317.6	114	1.0469	322.5	114	1.0511
303.0	129	1.0284	312.8	129	1.0362	317.7	129	1.0408	322.5	129	1.0448
303.1	144	1.0225	312.8	144	1.0307	317.8	144	1.0352	322.5	144	1.0390
332.4	9	1.1225	342.4	9	1.1310	352.6	9	1.1386			
332.4	24	1.1120	342.4	24	1.1199	352.7	24	1.1272			
332.5	39	1.1027	342.5	39	1.1102	352.9	39	1.1171			
332.6	54	1.0942	342.5	54	1.1012	353.0	54	1.1081			
332.5	69	1.0865	342.7	69	1.0932	352.8	69	1.0996			
332.5	84	1.0793	342.6	84	1.0859	352.8	84	1.0918			
332.5	99	1.0727	342.7	99	1.0789	352.6	99	1.0847			
332.6	114	1.0664	342.6	114	1.0723	352.6	114	1.0779			
332.5	129	1.0604	342.6	129	1.0662	352.7	129	1.0717			
332.6	144	1.0549	342.7	144	1.0605	352.7	144	1.0657			

which gave higher errors of 2.2% to 3.3% between calculated and experimental pressures. The Tait equation was found to provide the best correlation of the data among the equations tested.

It is often desired to correlated *PVT* data with equations that have a more theoretical basis and that can be used to derive other thermodynamic properties. For this purpose, we evaluated many equations of state which included the Peng−Robinson (1976), the Hederer−Peter−Wenzel equation (1976), a lattice equation (Kumar et al., 1987), the Flory equation (Flory et al., 1964), and the simplified perturbed hard chain theory (SPHCT) equation (Kim et al.,

Table 8. *PVT* for Coconut Oil (Fat)

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
294.2	9	1.0485	296.8	9	1.0563	298.6	9	1.0648	300.5	9	1.0780
294.5	24	1.0394	297.0	24	1.0464	298.8	24	1.0533	300.6	24	1.0652
294.4	39	1.0298	297.1	39	1.0358	298.7	39	1.0413	300.7	39	1.0506
294.4	54	1.0208	297.1	54	1.0260	298.6	54	1.0305	300.7	54	1.0376
294.4	69	1.0127	297.0	69	1.0172	298.6	69	1.0210	300.7	69	1.0266
294.4	84	1.0054	297.0	84	1.0094	298.7	84	1.0126	300.7	84	1.0173
294.5	99	0.9989	296.9	99	1.0024	298.7	99	1.0052	300.6	99	1.0092
294.4	114	0.9931	297.0	114	0.9962	298.6	114	0.9987	300.6	114	1.0020
294.3	129	0.9879	296.9	129	0.9907	298.6	129	0.9928	300.8	129	0.9957
294.4	144	0.9830	297.0	144	0.9856	298.7	144	0.9875	300.8	144	0.9901
302.9	9	1.0892	312.7	9	1.0969	332.7	9	1.1124	352.5	9	1.1275
302.8	24	1.0799	312.7	24	1.0870	332.6	24	1.1017	352.7	24	1.1157
303.0	39	1.0715	312.7	39	1.0783	332.8	39	1.0920	352.8	39	1.1053
303.0	54	1.0637	312.7	54	1.0703	332.8	54	1.0833	352.8	54	1.0960
303.0	69	1.0500	312.8	69	1.0629	332.7	69	1.0754	353.0	69	1.0875
303.1	84	1.0280	312.8	84	1.0561	332.8	84	1.0681	353.0	84	1.0798
303.1	99	1.0131	312.9	99	1.0498	332.8	99	1.0613	353.0	99	1.0726
303.0	114	1.0050	312.9	114	1.0439	332.8	114	1.0547	353.0	114	1.0659
303.0	129	0.9984	312.9	129	1.0383	332.8	129	1.0487	352.9	129	1.0589
302.9	144	0.9927	312.7	144	1.0312	332.8	144	1.0431	352.9	144	1.0529

Table 9. *PVT* for Palm Oil (Fat)

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
293.9	9	1.0536	298.2	9	1.0645	302.9	9	1.0875	312.5	9	1.0984
294.0	24	1.0441	298.3	24	1.0529	303.0	24	1.0739	312.6	24	1.0885
294.1	39	1.0354	298.4	39	1.0426	303.0	39	1.0594	312.5	39	1.0798
294.0	54	1.0278	298.4	54	1.0340	302.9	54	1.0460	312.6	54	1.0718
294.0	69	1.0209	298.3	69	1.0261	302.9	69	1.0352	312.6	69	1.0644
294.1	84	1.0145	298.4	84	1.0192	302.9	84	1.0263	312.5	84	1.0575
294.0	99	1.0086	298.4	99	1.0127	302.9	99	1.0186	312.6	99	1.0510
294.1	114	1.0032	298.2	114	1.0070	303.0	114	1.0118	312.6	114	1.0422
294.1	129	0.9981	298.3	129	1.0017	303.0	129	1.0057	312.6	129	1.0250
294.1	144	0.9929	298.4	144	0.9967	302.9	144	1.0002	312.8	144	1.0129
332.4	9	1.1140	352.7	9	1.1301						
332.4	24	1.1032	352.8	24	1.1182						
332.6	39	1.0936	353.0	39	1.1077						
332.7	54	1.0849	353.0	54	1.0984						
332.7	69	1.0771	353.1	69	1.0897						
332.6	84	1.0698	353.1	84	1.0819						
332.6	99	1.0630	353.2	99	1.0745						
332.7	114	1.0567	353.2	114	1.0678						
332.7	129	1.0508	353.2	129	1.0614						
332.6	114	1.0451	353.2	144	1.0554						

Table 10. *PVT* for Palm Kernel Oil (Fat)

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
295.2	9	1.0694	298.5	9	1.0858	303.4	9	1.1193	308.3	9	1.1237
295.3	24	1.0564	298.5	24	1.0705	303.4	24	1.1091	308.1	24	1.1128
295.4	39	1.0424	298.5	39	1.0525	303.5	39	1.0947	308.1	39	1.1033
295.4	54	1.0313	298.6	54	1.0382	303.5	54	1.0652	308.1	54	1.0947
295.4	69	1.0223	298.6	69	1.0277	303.5	69	1.0436	308.3	69	1.0787
295.3	84	1.0150	298.6	84	1.0194	303.4	84	1.0300	308.3	84	1.0511
295.3	99	1.0086	298.6	99	1.0122	303.4	99	1.0206	308.3	99	1.0333
295.3	114	1.0028	298.6	114	1.0060	303.4	114	1.0128	308.3	114	1.0221
295.4	129	0.9977	298.5	129	1.0005	303.3	129	1.0061	308.3	129	1.0135
295.4	144	0.9929	298.5	144	0.9955	303.4	144	1.0004	308.4	144	1.0065
313.3	9	1.1279	323.7	9	1.1361	332.6	9	1.1444	353.0	9	1.1624
313.2	24	1.1165	322.9	24	1.1249	332.7	24	1.1325	353.0	24	1.1493
313.2	39	1.1071	322.9	39	1.1148	332.7	39	1.1221	353.3	39	1.1379
313.2	54	1.0985	323.0	54	1.1058	332.7	54	1.1126	353.4	54	1.1277
313.2	69	1.0905	322.8	69	1.0975	332.7	69	1.1041	353.4	69	1.1185
313.2	84	1.0831	322.9	84	1.0897	332.9	84	1.0961	353.2	84	1.1099
313.2	99	1.0661	322.9	99	1.0827	332.8	99	1.0888	353.2	99	1.1019
313.3	114	1.0414	322.9	114	1.0760	332.8	114	1.0820	353.1	114	1.0945
313.4	129	1.0257	322.9	129	1.0697	332.8	129	1.0755	353.1	129	1.0878
313.2	144	1.0155	322.9	144	1.0637	332.9	144	1.0695	353.1	144	1.0813

1986). The equation of state constants, such as, a, b, and v^*, were used directly as fitting parameters since the critical properties for the components were unavailable. Only the Flory and SPHCT equations could provide a satisfactory fit of the data, as the other equations were unable to match the steep slope of the liquid isotherm. However, as the Flory equation was originally intended for polymers and does not reduce to the ideal gas limit, only the SPHCT equation is discussed further. Equation constants were determined, and summaries are given in Tables 19 and 20. The Tait and SPHCT equations can fit the data to within 1.3% and 2.3% average error in pressure, respectively. However, the Tait equation was fit to each isotherm whereas the parameters for the SPHCT equation were assumed to be temperature independent as stated in the original reference.

Table 11. *PVT* for Castor Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.0493[a]	312.8	0.1	1.0564[a]	332.6	0.1	1.0709[a]	352.6	0.1	1.0859[a]
303.1	9	1.0443	312.7	9	1.0510	332.6	9	1.0649	352.8	9	1.0793
303.1	24	1.0369	312.7	24	1.0432	332.7	24	1.0563	352.9	24	1.0698
303.0	39	1.0301	312.7	39	1.0360	332.7	39	1.0484	353.0	39	1.0614
303.1	54	1.0236	312.6	54	1.0294	332.7	54	1.0413	353.0	54	1.0538
303.1	69	1.0177	312.8	69	1.0230	332.7	69	1.0347	353.0	69	1.0466
303.1	84	1.0121	312.7	84	1.0172	332.7	84	1.0286	353.1	84	1.0402
303.1	99	1.0069	312.7	99	1.0118	332.7	99	1.0228	353.1	99	1.0340
303.1	114	1.0019	312.7	114	1.0067	332.7	114	1.0173	352.8	114	1.0281
303.1	129	0.9972	312.6	129	1.0018	332.8	129	1.0123	352.8	129	1.0226
303.1	144	0.9928	312.8	144	0.9972	332.7	144	1.0074	352.8	144	1.0174

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 12. *PVT* for Menhaden Fish Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.0843[a]	312.7	0.1	1.0916[a]	332.7	0.1	1.1068[a]	353.0	0.1	1.1237[a]
303.1	9	1.0783	312.7	9	1.0853	332.8	9	1.0999	352.9	9	1.1159
303.1	24	1.0697	312.7	24	1.0763	332.8	24	1.0901	352.8	24	1.1049
303.1	39	1.0618	312.7	39	1.0682	332.8	39	1.0812	353.2	39	1.0955
303.3	54	1.0546	312.7	54	1.0607	332.8	54	1.0730	353.3	54	1.0870
303.3	69	1.0477	312.8	69	1.0539	332.8	69	1.0656	353.0	69	1.0787
303.3	84	1.0413	312.9	84	1.0475	332.9	84	1.0591	353.1	84	1.0716
303.3	99	1.0352	312.9	99	1.0412	332.9	99	1.0528	353.3	99	1.0649
303.1	114	1.0298	312.7	114	1.0356	333.0	114	1.0469	353.4	114	1.0587
303.1	129	1.0248	312.7	129	1.0303	333.0	129	1.0414	353.2	129	1.0526
303.1	144	1.0200	312.9	144	1.0253	332.9	144	1.0361	353.2	144	1.0469

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 13. *PVT* for Linseed Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.0849[a]	312.7	0.1	1.0920[a]	332.3	0.1	1.1077[a]	352.4	0.1	1.1233[a]
303.1	9	1.0787	312.8	9	1.0857	332.4	9	1.1008	352.4	9	1.1157
303.1	24	1.0701	312.8	24	1.0766	332.5	24	1.0911	352.5	24	1.1048
303.1	39	1.0622	312.6	39	1.0684	332.7	39	1.0824	352.5	39	1.0953
303.1	54	1.0549	312.6	54	1.0610	332.7	54	1.0741	352.7	54	1.0864
303.1	69	1.0482	312.6	69	1.0541	332.6	69	1.0668	352.7	69	1.0783
303.1	84	1.0419	312.6	84	1.0476	332.7	84	1.0597	352.7	84	1.0708
303.0	99	1.0361	312.8	99	1.0415	332.6	99	1.0533	352.7	99	1.0639
303.1	114	1.0306	312.7	114	1.0358	332.7	114	1.0473	352.7	114	1.0577
303.1	129	1.0254	312.8	129	1.0305	332.7	129	1.0415	352.7	129	1.0515
303.1	144	1.0204	312.7	144	1.0254	332.7	144	1.0361	352.4	144	1.0457

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 14. *PVT* for Olive Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.1051[a]	312.8	0.1	1.1130[a]	332.6	0.1	1.1301[a]	352.6	0.1	1.1401[a]
303.1	9	1.0988	312.8	9	1.1062	332.6	9	1.1229	352.7	9	1.1380
303.1	24	1.0898	312.9	24	1.0968	332.7	24	1.1121	352.8	24	1.1267
303.3	39	1.0816	312.9	39	1.0883	332.7	39	1.1033	352.8	39	1.1168
303.1	54	1.0741	312.8	54	1.0803	332.7	54	1.0949	353.0	54	1.1077
303.1	69	1.0671	312.8	69	1.0731	332.8	69	1.0873	353.1	69	1.0993
303.3	84	1.0605	312.8	84	1.0664	332.7	84	1.0801	353.0	84	1.0919
303.3	99	1.0546	312.9	99	1.0603	332.7	99	1.0734	352.9	99	1.0848
303.3	114	1.0489	312.8	114	1.0543	332.8	114	1.0672	353.0	114	1.0781
303.3	129	1.0434	312.8	129	1.0489	332.8	129	1.0614	353.0	129	1.0719
303.3	144	1.0384	312.7	144	1.0437	332.9	144	1.0557	353.0	144	1.0660

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Parameter Generalization

The SPHCT equation provided the best correlation of the data of the theoretical equations tested and so its parameters, T^*, v^*, and "c" were generalized. The form of the equation is

$$P = RT/v(1 + cz^{\mathrm{rep}}) - cRTZ_{\mathrm{M}}v^*Y/(v + v^*Y) \qquad (2)$$

where

$$z^{\mathrm{rep}} = (4\tau v^*/v - 2(\tau v^*/v)^2)/(1 - \tau v^*/v)^3 \qquad (3)$$

and

$$Y = \exp(T^*/2T) - 1 \qquad T^* = \epsilon q/ck \qquad v^* = N_{\mathrm{A}}s\sigma^3/\sqrt{2} \qquad (4)$$

In eqs 2–4, $Z_{\mathrm{M}} = 36$ and $\tau = 0.7405$, as recommended in the original reference. To develop a generalized form of the parameters in terms of the properties in Table 1, we considered the following. The saponification value (SV) indicates the molecular weight or size of the fats or oils. The iodine value (IV) is related to the molecular weight and to the degree of unsaturation. Although a number of

Table 15. *PVT* for Perilla Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.3	0.1	1.0841[a]	312.8	0.1	1.0932[a]	332.6	0.1	1.1087[a]	352.9	0.1	1.1244[a]
303.1	9	1.0782	312.9	9	1.0870	332.7	9	1.1018	353.1	9	1.1167
303.3	24	1.0697	313.0	24	1.0781	332.7	24	1.0919	353.0	24	1.1057
303.3	39	1.0618	312.9	39	1.0700	332.8	39	1.0832	353.0	39	1.0961
303.1	54	1.0546	312.9	54	1.0627	332.7	54	1.0751	353.2	54	1.0875
303.1	69	1.0479	313.0	69	1.0558	332.9	69	1.0677	353.4	69	1.0797
303.1	84	1.0417	312.9	84	1.0494	332.8	84	1.0608	353.5	84	1.0725
303.1	99	1.0359	312.9	99	1.0434	332.9	99	1.0545	353.4	99	1.0657
303.3	14	1.0304	312.9	114	1.0377	332.9	114	1.0484	353.5	114	1.0593
303.3	129	1.0252	312.9	129	1.0325	332.9	129	1.0427	353.5	129	1.0533
303.1	144	1.0203	312.8	144	1.0274	332.8	144	1.0373	353.4	144	1.0476

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 16. *PVT* for Safflower Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.1	0.1	1.0912[a]	312.5	0.1	1.0989[a]	332.5	0.1	1.1142[a]	352.5	0.1	1.1297[a]
333.0	9	1.0851	312.7	9	1.0925	332.6	9	1.1072	352.5	9	1.1220
303.1	24	1.0763	312.8	24	1.0833	332.6	24	1.0971	352.6	24	1.1111
303.1	39	1.0683	312.7	39	1.0749	332.6	39	1.0882	352.8	39	1.1015
303.1	54	1.0610	312.7	54	1.0673	332.7	54	1.0802	352.7	54	1.0926
303.1	69	1.0542	312.7	69	1.0603	332.7	69	1.0727	352.8	69	1.0845
303.1	84	1.0480	312.9	84	1.0538	332.7	84	1.0656	352.9	84	1.0772
303.1	99	1.0420	312.9	99	1.0477	332.7	99	1.0592	352.8	99	1.0704
303.1	114	1.0365	312.9	114	1.0420	332.7	114	1.0531	353.2	114	1.0642
303.1	129	1.0312	312.9	129	1.0367	332.6	129	1.0473	353.2	129	1.0581
303.1	144	1.0263	313.0	144	1.0315	332.8	144	1.0418	353.3	144	1.0524

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 17. *PVT* for Sesame Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
302.8	0.1	1.0961[a]	312.5	0.1	1.1036[a]	332.4	0.1	1.1195[a]	352.5	0.1	1.1359[a]
302.8	9	1.0898	312.5	9	1.0970	332.4	9	1.1122	352.6	9	1.1279
302.8	24	1.0808	312.5	24	1.0876	332.5	24	1.1019	352.8	24	1.1166
302.8	39	1.0726	312.6	39	1.0790	332.6	39	1.0926	352.9	39	1.1066
302.9	54	1.0653	312.7	54	1.0713	332.6	54	1.0843	354.0	54	1.0975
302.8	69	1.0584	312.6	69	1.0640	332.5	69	1.0766	353.9	69	1.0892
302.9	84	1.0520	312.7	84	1.0574	332.5	84	1.0695	354.0	84	1.0816
302.9	99	1.0459	312.7	99	1.0510	332.6	99	1.0629	354.0	99	1.0744
302.9	14	1.0401	312.6	114	1.0452	332.7	114	1.0567	353.9	114	1.0686
303.0	129	1.0346	312.7	129	1.0396	332.7	129	1.0508	354.0	129	1.0624
303.0	144	1.0294	312.6	144	1.0345	332.6	144	1.0453	354.0	144	1.0566

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

Table 18. *PVT* for Soybean Oil

T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}	T/K	P/MPa	V/cm^3·g^{-1}
303.0	0.1	1.0952[a]	312.7	0.1	1.1021[a]	332.6	0.1	1.1175[a]	352.6	0.1	1.1334[a]
303.1	9	1.0891	312.7	9	1.0956	332.6	9	1.1103	352.7	9	1.1254
303.1	24	1.0802	312.7	24	1.0865	332.7	24	1.1001	352.8	24	1.1142
303.1	39	1.0721	312.8	39	1.0780	332.7	39	1.0910	352.8	39	1.1043
303.1	54	1.0647	312.8	54	1.0704	332.7	54	1.0827	353.0	54	1.0955
303.1	69	1.0577	312.8	69	1.0633	332.8	69	1.0751	353.1	69	1.0873
303.1	84	1.0512	312.9	84	1.0567	332.7	84	1.0681	353.0	84	1.0798
303.1	99	1.0452	312.9	99	1.0505	332.7	99	1.0615	352.9	99	1.0729
303.1	114	1.0395	312.8	114	1.0447	332.8	114	1.0555	353.0	114	1.0663
303.1	129	1.0341	312.8	129	1.0392	332.8	129	1.0497	353.0	129	1.0603
303.1	144	1.0286	312.8	144	1.0340	332.9	144	1.0443	353.0	144	1.0545

[a] Volumetric values at 0.1 MPa are extrapolated from high-pressure data. See text for explanation.

other properties such as melting point and boiling point were considered, these two properties were found to be the most appropriate. Using all of the oil and liquid fat data, a multivariate regression was performed with the SAS statistical package (SAS, 1993) to determine SPHCT parameters T^*, v^*, and "c" in terms of the saponification value, the iodine value, and their interaction and quadratic effects. The v^* were found to correlate with the saponification value; T^* and "c" were found to correlate with the iodine value and temperature. The final equations obtained were

$$v^*/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = 1221.87 - 2.708\mathrm{SV} \qquad (5)$$

$$c = 17.4484 - 0.01416\mathrm{IV} - 0.0142T/\mathrm{K} \qquad (6)$$

$$T^*/\mathrm{K} = 414.30 + 0.4169\mathrm{IV} \qquad (7)$$

Equations 2−7 provide a generalized equation of state that can reproduce the oil data to within the following absolute average percent deviations in pressure: olive (1.96%), sesame (3.25%), soybean (4.07%), safflower (3.67%), fish (8.14%), perilla (4.83%), and linseed (8.57%), or an overall average of about 4.9%.

Conclusions

A number of data have been reported for fats and oils. The *PVT* behavior of the oils can be grouped according to fatty acid composition. The fats exhibit various degrees of crystallinity which is affected by temperature and pressure. The Tait and SPHCT equations were found to be the best empirical and theoretical correlating equations, respectively. SPHCT parameters, v^*, T^*, and "c" could only be generalized for the oil components.

Table 19. Model Parameters

		Tait $c = -0.07325$	SPHCT (fit to all temperatures)		
substance	T/K	B	V^*/cm^3·mol^{-1}	T^*/K	c
olive	303	113.67	709.72	456.7	11.16
	313	109.36			
	333	100.05			
	353	91.34			
castor	303	134.41	724.08	497.9	11.28
	313	126.74			
	333	116.15			
	353	106.56			
sesame	303	113.14	712.04	496.5	9.72
	313	108.04			
	333	98.90			
	353	90.88			
soybean	303	114.3	716.52	496.4	9.78
	313	110.18			
	333	100.33			
	353	91.53			
safflower	303	115.87	705.07	487.5	10.08
	313	110.83			
	333	102.29			
	353	94.11			
fish	303	116.47	694.36	479.1	10.34
	313	112.57			
	333	103.71			
	353	93.88			
perilla	303	118.25	691.8	470.5	10.67
	313	114.25			
	333	103.62			
	353	94.17			
linseed	303	115.99	699.02	477.7	10.39
	313	112.00			
	333	103.48			
	353	93.64			
triolein	303	112.73	722.91	487.9	10.10
	313	108.75			
	333	100.11			
	353	90.76			
coconut	313	103.21	527.47	477.7	7.21
	333	94.16			
	353	85.69			
palm	313	104.32	554.04	463.8	7.89
	333	94.62			
	353	85.37			
palm kernel	323	90.55	523.29	429.6	8.03
	333	86.07			
	353	77.84			
beef tallow	333	98.57	693.28	463.9	10.18
	343	93.56			
	353	90.68			
beef shank	333	96.49	639.41	484.34	8.73
	343	91.98			
	353	89.53			
trilaurin	333	91.24	515.73	482.8	6.66
	343	87.69			
	353	83.92			

Table 20. Errors for Tait and SPHCT Equations[a]

	Tait		SPHCT	
substance	AAPD	BIAS	AAPD	BIAS
trilaurin	1.352	−0.253	1.957	−1.531
triolein	1.180	−0.188	2.452	−3.404
beef shank	2.787	−0.243	1.647	−1.320
beef tallow	1.256	−0.174	1.807	−1.607
coconut	1.389	−0.254	2.260	−2.098
palm	1.022	−0.133	2.114	−1.537
palm kernel	1.578	−0.341	1.883	−1.566
castor	1.039	−0.149	2.511	−3.559
fish	1.144	−0.188	2.375	−3.676
linseed	1.188	−0.207	2.610	−3.897
olive	1.141	−0.173	2.554	−4.321
perilla	1.119	−0.165	3.777	−9.911
safflower	1.034	−0.146	2.292	−2.912
sesame	1.091	−0.159	2.309	−3.170
soybean	1.172	−0.190	2.489	−3.472
average	1.299	−0.197	2.336	−3.199

[a] AAPD = $1/N\sum|P^{\text{calc}} - P^{\text{exp}}|/P^{\text{exp}}100\%$. BIAS = $1/N\sum(P^{\text{calc}} - P^{\text{exp}})100\%$.

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Literature Cited

Acosta, G. M. Solubility, High Pressure Phase Behavior, and Solid-Liquid Equilibria of Fats and Oils. Experimental Measurements and Model Development for Triglyceride Systems. Ph.D. Thesis, University of South Carolina, Columbia, South Carolina, 1995.

Acosta, G. M.; Smith, Jr., R. L.; Walsh, J. E.; Boni, K. A. Beef Shank Fat Solubility in Supercritical Carbon Dioxide-Propane Mixtures and in Liquid Propane. *J. Food Sci.* **1995**, *60* (5), 983−987.

Ashour, I.; Hammam, H. Equilibrium Solubility of Pure Mono-, Di-, and Trilaurin in Supercritical Carbon Dioxide- Experimental Measurements and Model Prediction. *J. Supercrit. Fluids* **1993**, *6*, 3−8.

Bamberger, T.; Erickson, J. C.; Cooney, C. L. Measurement and Model Prediction of Solubilities of Pure Fatty Acids, Pure Triglycerides, and Mixtures of Triglycerides in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1988**, *33* (3), 327−333.

Bharath, R.; Inomata, H.; Adschiri, T.; Arai, K. Phase Equilibrium Study for the Separation and Fractionation of Fatty Oil Components using Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1992**, *81*, 307−320.

Fakhreddine, Y. A.; Zoller, P. Thermophysical Properties of Azomethine Ether Main-Chain Liquid Crystalline Polymers at Pressures to 200 MPa. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32* (15), 2445−2459.

Flory, P. J.; Orwoll, R. A.; Vrij, A. Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3507−3520.

Halvorsen, J. D.; Mammel, W. C.; Clements, L. D. Density Estimation for Fatty Acids and Vegetable Oils Based on their Fatty Acid Composition. *J. Am. Oil Chem. Soc.* **1993**, *70*, 875−880.

Hederer, H.; Peter, S.; Wenzel, H. Calculation of Thermodynamic Properties from a Modified Redlich-Kwong Equation of State. *Chem. Eng. J.* **1976**, *11*, 183−190.

Kim, C.; Vimalchand, P.; Donohue, M. D.; Sandler, S. I. Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed Hard Chain Theory. *AIChE J.* **1986**, *32* (1), 1726−1734.

King, J. W.; Johnson, J. H.; Friedrich, J. P. Extraction of Fat Tissue from Meat Products with Supercritical Carbon Dioxide. *J. Agric. Food Chem.* **1989**, *37*, 951−954.

Krogh, F. T. Efficient Algorithms for Polynomial Interpolation and Numerical Differentiation. *Math. Comp.* **1970**, *24*, 185−190.

Kumar, S. K.; Suter, U. W.; Reid, R. C. A Statistical Mechanics Based Lattice Model Equation of State. *Ind. Eng. Chem. Res.* **1987**, *26*, 2532−2542.

Ohgaki, K.; Tsukahara, I.; Semba, K.; Katayama, T. A Fundamental Study of Extraction with a Supercritical Fluid. Solubilities of α-Tocopherol, Palmitic Acid, and Tripalmitin in Compressed Carbon Dioxide at 25 C and 40 C. *Int. Chem. Eng.* **1989**, *29* (2), 302−308.

Ollivon, M.; Perron, R. Measurement of Enthalpies and Entropies of Unstable Crystalline Forms of Saturated Even Monoacid Triglycerides. *Thermochim. Acta* **1982**, *53*, 183−194.

Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

SAS Institute Inc. SAS/STAT software, Version 6.08, Cary, North Carolina, 1993.

Stahl, E.; Quirin, K. W.; Gerard, D. Dense Gases for Extraction and Refining; Springer-Verlag: Berlin, 1988.

Swern, D. Bailey's Industrial Oils and Fats Products, 4th ed.; John Wiley & Sons: New York, 1979; Vol. 1.

Tilly, K. D.; Chaplin, R. P.; Foster, N. R. Supercritical Fluid Extraction of the Triglycerides Present in Vegetable Oils. *Sep. Sci. Technol.* **1990**, *25*, 357−367.

Vargaftik, N. B. Handbook of Physical Properties of Liquids and Gases; Hemisphere Publishing Corp.: New York, 1975.

Wesdorp, L. H. Liquid - Multiple Solid Phase Equilibria in Fats - theory and experiments. Ph.D. Thesis, University of Technology, Delft, Netherlands, 1990.

Zoller, P.; Bolli, P.; Pahud, V.; Ackermann, H. Apparatus for Measuring Pressure-Volume-Temperature Relationships of Polymers to 350 °C and 2200 kg/cm^2. *Rev. Sci. Instrum.* **1976**, *47* (8), 948−952.

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