Thermal and Flow Properties of Oils from Salmon Heads

Subramaniam Sathivel*

Fishery Industrial Technology Center, University of Alaska Fairbanks, Kodiak, Alaska 99615

ABSTRACT: Thermal and flow properties of unrefined oils from the heads of red or pink salmon were evaluated. Major thermal degradation of the salmon oils occurred between 200 and 450°C. Red and pink salmon oils were completely decomposed at 533 and 668°C, respectively. The phase transition of salmon oils occurred over a wide range of temperatures. The melting points of −69.6 to −0.36°C and −64.7 to 20.8°C were observed for red and pink salmon oils, respectively. The enthalpy was 40 J/g for red salmon oil and 39 J/g for pink salmon oil. Specific heat capacity ranges of 0.8 to 1.6 and 1.3 to 2.3 J/g/°C were observed for red and pink salmon oils, respectively. Both salmon oils exhibited Newtonian flow behavior. Red salmon oil required higher magnitudes of energy (kJ·mol^{-1}) to flow than pink salmon oil. The viscosity of salmon oils was temperature-dependent and could be predicted by the Arrhenius equation.

Paper no. J10985 in *JAOCS 82*, 147–152 (February 2005).

KEY WORDS: Enthalpy, melting point, rheology, salmon oil, specific heat capacity, thermal degradation.

About 50,000 to 80,000 metric tons of salmon heads was produced as a by-product from the processing of both pink (*Oncorhynchus gorbuscha*) and red salmon (*O. nerka*) in Alaska. Much of the oil in the salmon is found in the head, which contains approximately 15–18% lipids. Salmon oil contains a high concentration of n-3 FA, which play an important role in human health. Alaska fish processors annually produce approximately 20,000 metric tons of unrefined fish oil from about 2,000,000 metric tons of fish processed in Alaska. Information on thermal stability, m.p., specific heat capacity, enthalpy, and rheological properties of salmon oil is not available. Thermal and rheological analyses may define the quality of the oil and provide useful information necessary for designing the purification steps for unrefined salmon oil.

Thermal analysis measures some physical or chemical change, such as sample weight or specific heat, in materials as a function of temperature. Use of thermal analysis, a thermogravimetry (TG) analyzer, and DSC for oil and fat characterization has gained much interest from the food industries. These methods require less time and provide precise stability data (1). Sathivel *et al.* (2) reported that TG analysis could be used to determine the quality of fish oils at different refining steps. Wesolowski and Erecinska (1) found that TG analysis was very useful in defining the quality of rapeseed oils compared with

chemical analysis. Hassel (3) reported that TG analysis was an alternative method of measuring stability in vegetable oils and that it required less time for quality control. Compared with older techniques such as the active oxygen method or the oxygen bomb method (4), the TG method offers the advantages of a smaller requisite sample size for analysis, precision, and the ability to evaluate the continuous oxidation process. DSC offers a simple means to investigate characteristics of m.p. and freezing points of fats. The influence of fat composition, water content, production materials, aging, and heat treatment on fat and oil quality can be demonstrated on the basis of DSC investigation. DSC has been used to characterize the thermal conductivity and specific heat (5), melting and crystallization (6,7), oil content (8), wax coating (7), and phase transition (9) of foods.

Knowledge of rheological properties helps solve problems related to the transfer or movement of bulk quantities of the liquid (10). At low temperatures, impurities of a crude oil tend to precipitate on the walls of pipes. Some solid particles in the bulk flow increase the viscosity of the oil, causing an increased pressure drop in the pipeline. As a result of increased viscosity, the oil flow properties exhibit non-Newtonian behavior. The fish oil refining process involves degumming, neutralizing, bleaching, and deodorizing. Impurities, such as FFA, proteins, moisture, pigments, and volatile flavors, are sequentially removed from the oil (11). Removing impurities may change the flow properties of the oil (12).

Knowledge of the thermal and rheological properties of the salmon head oils is essential for the design of proper unit operations, production cost analysis, and final quality evaluation. The objective of this study was to evaluate the thermal stability, m.p., specific heat capacity, enthalpy, and rheological properties of oils from red and pink salmon heads.

EXPERIMENTAL PROCEDURES

Samples and sample preparation. Red and pink salmon heads were obtained in three separated batches from a local fish processing plant in Kodiak, Alaska. The heads were frozen at −40°C until used. The thawed salmon heads were finely ground in a Butcher-Boy grinder (Model A42.30; Lasar Mfg. Corp., Los Angeles, CA). Water was added (water/minced head, 2:1 vol/wt), and the mixture was heated at 70°C for 45 min. The solid particles were separated from the liquid phase by filtering through cheesecloth, and the particles were pressed to remove most of the liquid. The crude oil was separated from the water phase and solid particles by centrifuging at 10,242 × *g* for 30 min. The resulting crude oil was collected and stored at −40°C

*Address correspondence at Fishery Industrial Technology Center, University of Alaska Fairbanks, 118 Trident Way, Kodiak, AK 99615.
E-mail: sathivel@sfos.uaf.edu

until used. Three experimental crude oil extractions were conducted.

Proximate composition. The ground red and pink salmon heads were analyzed in triplicate for moisture and ash contents using AOAC standard methods 930.15 and 942.05, respectively (13). The fat content of salmon heads was determined using dichloromethyl ether on an automated ASE-200 fat extractor (Dionex Corporation, Sunnyvale, CA). The nitrogen content for salmon heads samples was determined in triplicate using the LECO FP-2000 Nitrogen Analyzer (LECO Corp., St. Joseph, MI). The protein content was calculated as percent nitrogen times 6.25.

Color, bulk density, and water activity (a_w). The color of salmon oil samples was determined using the Minolta Chromameter (Model CR-300; Minolta Co., Ltd., Osaka, Japan), and an average of six determinations was reported as L*, a*, and b* values. The bulk density of salmon oil samples was determined in triplicate using a 25-mL glass measuring cylinder. Samples were filled to 25 mL, the weight-to-volume ratios determined, and bulk density values reported as g per mL. An AquaLab water activity meter (Model Series 3TE; Decagon Devices, Inc., Pullman, WA) was used to measure the a_w of the salmon oil samples at 25°C.

Thermal analysis. Thermal stability of the crude salmon oils was analyzed using the Thermogravimetric Analyzer (Model Q50; TA Instruments, New Castle, DE). Approximately 1–1.2 mg of each sample was added to an aluminum pan, the pan was placed in the furnace, and the exact sample weight was determined. The sample was heated to 700°C under an air atmosphere at the rate of 5°C/min. Sample weight differences were automatically recorded every 0.5 s. Collected data were analyzed and plotted using TA Universal Analyzer Software. The graphs were normalized based on a sample weight basis.

DSC analysis. The DSC experiments were conducted using a differential scanning calorimeter (Model DSC 2920; TA Instruments). Approximately 0.5–1 mg of each salmon oil sample was placed in the aluminum sample vessel. The sample vessel was then placed on the sample platform, and an empty aluminum vessel was placed on the reference platform. To determine the phase transition of the salmon oil samples, a linear heating rate of 5°C/min over a temperature range of –75 to 100°C was used. The thermogram peak was used to provide an estimate of enthalpy *(ΔH)*. The thermogram peak points were used to determine the m.p. The TA Instrument Software was used to calculate the specific heat capacity from the DSC transition curve.

Flow properties measurements. Rheological properties of the salmon oil samples were measured in triplicate using an AR 2000 Rheometer (TA Instruments) fitted with a plate geometry (acrylic plates with a 60-mm diameter having a 1000-µm gap between the two plates). Each sample was placed in the temperature-controlled parallel plate and allowed to equilibrate to –4, 0, or 24°C. Shear stress was measured at –4, 0, and 24°C at varying shear rates from 0 to 500 s^{-1}. The mean values of triplicate samples were reported.

The power law (Eq. 1) was used to analyze the flow behavior index of the salmon oil samples,

$$\sigma = K\gamma^n \quad\quad [1]$$

where σ = shear stress (Pa·s), γ = shear rate (s^{-1}), K = consistency index (Pa·s^n), and n = flow behavior index. Logarithms were taken on both sides of Equation 1, and a plot of log σ vs. log γ was constructed. The resulting straight line yielded the magnitude of log *K* (i.e., intercept) and *n* (i.e., slope).

The effect of temperature on viscosity was described through the Arrhenius relationship shown in Equation 2 (14),

$$\mu_a = \mu_{\infty A} \exp (E_a/RT) \quad\quad [2]$$

where μ_a is the viscosity at a specific shear rate, $\mu_{\infty A}$ is the frequency factor, E_a is the activation energy (J·mol^{-1}), R is the gas constant (J·mol^{-1}), and T is the temperature (K). Viscosity (μ_a) of the salmon oil samples was measured at –4, 0, 4, 8, 12, 16, 20, and 24°C at a shear rate of 500 s^{-1} by using the AR 2000 Rheometer. A plot of ln μ_a (viscosity) vs. 1/*T* (1/absolute temperature) was constructed for each salmon oil sample. The slope of the straight line, the intercept, and the regression coefficient were calculated using the trend line of the plot. The magnitude of E_a was calculated as the slope of the plot multiplied by the gas constant, and $\mu_{\infty A}$ was an exponential of the intercept. Viscosities of salmon oil samples were predicted at 3, 6, 9, 12, 15, 18, and 21°C by using Equation 2 with calculated values of E_a/R and $\mu_{\infty A}$. Viscosity (μ_a) of the salmon oil samples was measured at 3, 6, 9, 12, 15, 18, and 21°C at a shear rate of 500 s^{-1} by using the AR 2000 Rheometer and compared with the predicted viscosity of the salmon oil samples.

Statistical analysis. ANOVA was conducted to evaluate the significance of observed differences among treatment means (SAS version 8.2, SAS Institute Inc., Cary, NC), followed by the *post hoc* Tukey's Studentized range test (15).

RESULTS AND DISCUSSION

Proximate composition of salmon heads. The proximate composition of red and pink salmon heads is given in Table 1. The red and pink salmon heads contained 69.6 and 72.4% moisture, respectively. The protein content of pink salmon heads was higher (14.1%) than that of red salmon heads (11.9%). The fat content of red salmon heads (14.5%) was significantly (*P* < 0.05) higher than that of pink salmon heads (9.3%).

Color, bulk density, and water activity (a_w) *of unrefined salmon oils.* The color analysis of salmon oils is given in Table 2. Oil from red salmon was darker red (lower L* and higher a* values) than oil from pink salmon. Red salmon oil was less yellowish (b* = 14.6) than pink salmon oil (b* = 16.6). Bulk density is important in the storage of fish oil, and the red salmon oil bulk density (0.9 g/mL) was significantly (*P* < 0.05) higher (0.81 g/mL) than that of pink salmon oil (Table 2). The a_w of red salmon oil (0.57) was slightly higher (*P* < 0.05) than that of pink salmon oil (0.53) (Table 2).

Thermal analysis of unrefined salmon oils. The TG curves (Fig. 1) show the thermal decomposition of pink and red salmon oils. Between 200 and 450°C, weight loss of both red and pink salmon oils increased with increasing heating temperature. The
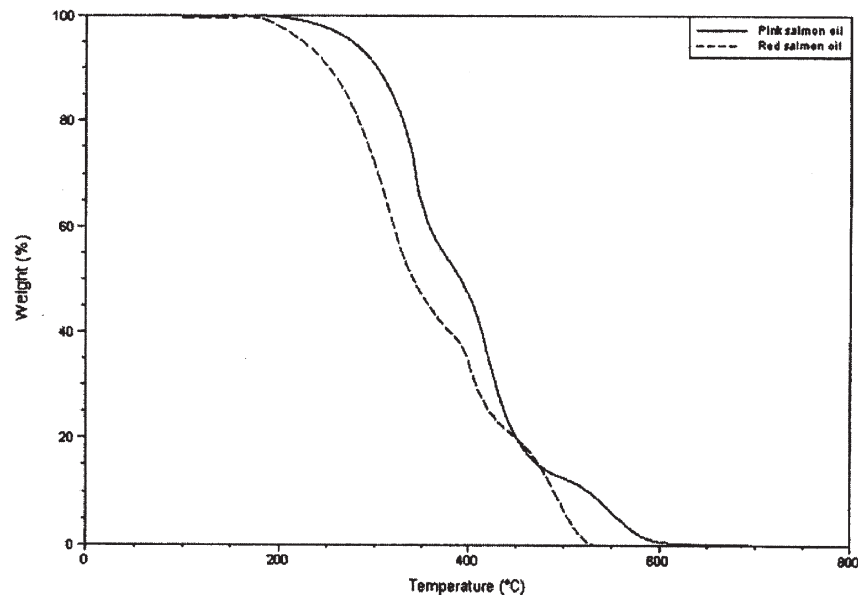
FIG. 1. Thermogravimetric curves of the unrefined red and pink salmon oils in the air atmosphere.

TABLE 1
Proximate Composition[a] of Red and Pink Salmon Heads

Composition (%)	Red	Pink
Protein	11.9 ± 0.7[b]	14.1 ± 0.3[a]
Fat	14.5 ± 2.0[a]	9.3 ± 0.5[b]
Moisture	69.6 ± 2.7[a]	72.4 ± 0.4[a]
Ash	4.0 ± 0.3[a]	4.2 ± 0.1[a]

[a]Values are means ± SD of three determinations. Means with the same superscript letter in each row are not significantly different ($P > 0.05$). Red = red salmon head; Pink = pink salmon head.

weight reduction was drastic between 200 and 450°C for both salmon oils. In an oxygen atmosphere, the onset of oil oxidation is characterized by oxygen absorption by the FA chain, leading to a formation of oxidation products known as peroxides. This behavior is usually identified by an increase in the initial sample mass (3). No weight gain was observed in the TG curves for both salmon oils that were analyzed under an air atmosphere, indicating that thermal decomposition of the oils was not related to oxygen absorption. Sathivel *et al.* (2) reported a similar result in that no weight gain for catfish and menhaden oils was observed under a nitrogen atmosphere. The weight loss between 100 and 200°C, 200 and 350°C, 350 and 450°C, and 450 and 500°C was 2.2, 51,

27.1, and 12.4% for red salmon oil, respectively, whereas it was 0.31, 36, 44.1, and 7.6% for pink salmon oil, respectively. The red salmon oil sample was decomposed at 533°C, whereas the pink salmon oil was decomposed at 668°C. This difference may be due to the presence of impurities in the pink salmon oils. Unrefined oils contain soluble impurities such as phospholipids, complexed metals and minerals (notably iron, calcium, and magnesium), FFA, and peroxides and their breakdown products, which are highly interactive with the oil (11). Sathivel *et al.* (16) reported that mineral content, FFA, and a_w of crude catfish oil decreased during the refining process. The presence of impurities reduces the effectiveness of heat transfer to unrefined oils and therefore results in less available energy for evaporating the volatiles. The weight loss of edible oils owing to thermal decomposition is higher in refined oils than in crude or unrefined oils. The higher value of the initial temperature of decomposition implies a better quality of oil (1). Sathivel *et al.* (2) reported that refining catfish and menhaden oils tended to reduce their relative resistance to thermal decomposition.

DSC analysis of unrefined salmon oils. The DSC thermograms (Figs. 2, 3) show two distinct endothermic peaks for red and pink salmon oils. The m.p. of red salmon oil ranged from –69.6 to –0.36°C, whereas the m.p. of pink salmon oil ranged

TABLE 2
Color L*a*b* Values, Bulk Density, and Water Activity of Unrefined Oils from the Heads of Red Salmon and Pink Salmon[a]

Oil samples	L*	a*	b*	Bulk density (g/mL)	Water activity (a_w)
Red	32.1 ± 2.0[b]	4.9 ± 0.3[a]	14.6 ± 0.7[b]	0.90 ± 0.02[a]	0.57 ± 0.01[a]
Pink	40.3 ± 2.3[a]	2.7 ± 0.1[b]	16.6 ± 0.8[a]	0.81 ± 0.01[b]	0.53 ± 0.01[b]

[a]Values are means ± SD of six determinations for L*, a*, and b* and of three determinations for bulk density and water activity. Means with the same superscript letter in each column are not significantly different ($P > 0.05$). Red = red salmon oil; Pink = pink salmon oil.
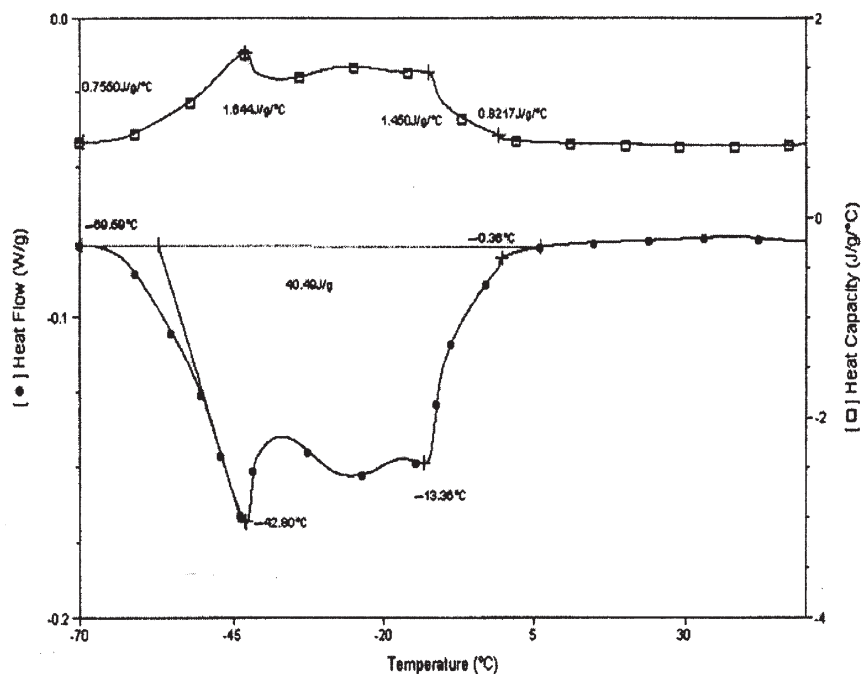
FIG. 2. The DSC thermogram of unrefined red salmon oil.

from −64.7 to 20.8°C. The negative m.p. of salmon oil were attributed to the presence of unsaturated FA (17). The peaks at −13.4°C for red salmon oil and at −8.8°C for pink salmon oil were not sharp. Sathivel (17) reported that purified FA and refined fish oil showed sharp and narrow peaks in the DSC thermograms, whereas the unrefined fish oil showed broad peaks. The m.p. of fish oil were sharper after each purification step that removed impurities from the oil (17).

The enthalpies for red and pink salmon oil were 40 and 39 J/g, respectively. The enthalpy values of salmon oils were slightly lower than those reported by Sathivel (17) for catfish oils (84.7 to 73.9 J/g). The specific heat capacity for red salmon oil ranged from 0.8 to 1.6 J/g/°C, whereas for pink salmon oil it was 1.3 to 2.3 J/g/°C. A phase transition is associated with enthalpy (18), which explains whether an oil changes from one physical state to another state either by
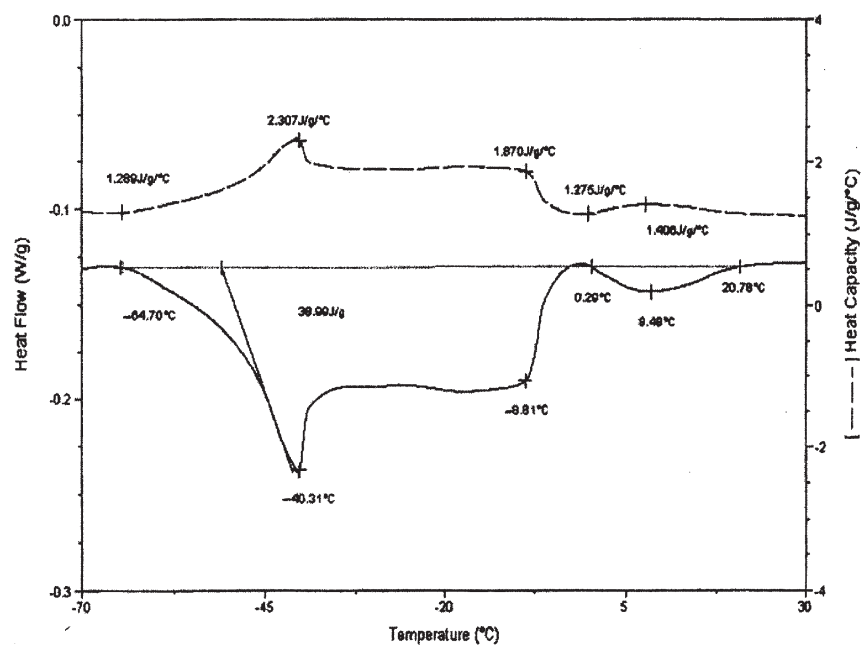

FIG. 3. The DSC thermogram of unrefined pink salmon oil.

TABLE 3
Flow Behavior Index, Consistency Index, and Arrhenius Parameters of Red and Pink Salmon Oils[a]

Temperature (°C)	Red salmon oil		Pink salmon oil	
	n	K (Pa·s)^n	n	K (Pa·s)^n
−4	0.99 ± 0.01[a]	0.2 ± 0.0[a]	0.99 ± 0.01[a]	0.2 ± 0.0[a]
0	1.0 ± 0.01[a]	0.13 ± 0.06[b]	0.99 ± 0.01[a]	0.1 ± 0.0[b]
4	1.0 ± 0.01[a]	0.1 ± 0.01[b,c]	1.0 ± 0.0[a]	0.09 ± 0.0[c]
8	1.0 ± 0.01[a]	0.08 ± 0.01[b,c,d]	1.0 ± 0.0[a]	0.07 ± 0.0[d]
12	1.0 ± 0.01[a]	0.07 ± 0.01[c,d]	1.0 ± 0.01[a]	0.06 ± 0.0[e]
16	1.0 ± 0.00[a]	0.05 ± 0.0[c,d]	0.99 ± 0.01[a]	0.05 ± 0.0[f]
20	1.0 ± 0.01[a]	0.04 ± 0.01[c,d]	1.0 ± 0.01[a]	0.04 ± 0.01[g]
24	1.0 ± 0.01[a]	0.03 ± 0.01[d]	0.99 ± 0.01[a]	0.04 ± 0.0[g]
E_a (J·mol^{-1})	36958.2 ± 1160.8[a]		30231.6 ± 206.6[b]	
$\mu_{\infty A}$	1.153E-8 ± 5.2E-9[b]		1.69E-7 ± 7.8E-9[a]	

[a]Values are means ± SD of three determinations. Means with the same letter in each *column* for red and pink salmon oils are not significantly different ($P > 0.05$). Means with the same letter in each *row* for E_a and $\mu_{\infty A}$ are not significantly different ($P > 0.05$). n = flow behavior index; K = consistency index; E_a = activation energy; $\mu_{\infty A}$ = the frequency factor.

absorbing (endothermic) or releasing (exothermic) heat. Specific heat capacity is an important measure that provides information about the amount of energy that must be supplied or withdrawn to change the temperature by a given amount. Information on the thermal degradation, m.p., specific heat capacity, and enthalpy of unrefined oils gives useful information for designing the process and optimizing unit operations for each salmon oil purification step.

Flow properties of unrefined salmon oils. The power law parameters for the red and pink salmon oils samples at −4, 0, 4, 8, 12, 16, 20, and 24°C are given in Table 3. The flow behavior index (n) of the oil samples was equal to 1.0 for both oil samples, which indicated that they were Newtonian fluids. The consistency index (K) values for red and pink salmon oil samples were higher at lower temperatures. The K value for the red and pink salmon oils at −4°C was 0.2 (Pa·s), and it was 0.1 and 0.09 (Pa·s)^n for red and pink salmon oil samples at 4°C, respectively. More than a fivefold increase in the magnitude of the K values for both oils between 20 and −4°C was observed, and this should be considered in the design of handling systems for

operation at low temperatures. At a given temperature, the n and K values of the red and pink salmon oils were similar. The K value is identically equal to the viscosity of the fluid (14).

The Arrhenius relationship (Eq. 2) was used to calculate the average magnitudes of activation energy of the red and pink salmon oil samples from the linear regression analysis of $1/T$ and the natural logarithm of the viscosity (Fig. 4). The magnitudes of E_a and $\mu_{\infty A}$ for red and pink salmon oil samples are given in Table 3. The magnitude of E_a was found to be 37 kJ·mol^{-1} for red salmon oil, which was higher than that of the pink salmon oil (30 kJ·mol^{-1}). The E_a indicates the energy barrier that must be overcome before the elementary flow process can occur (14). The K values between 0 and 12°C for red salmon oil were slightly higher than those of pink salmon oil. Samples having higher viscosities resulted in higher magnitudes of activation energy (19). Figure 5 illustrates the data from the predicted viscosity (Eq. 2) and the experimental viscosity for the red salmon and pink salmon oil samples.

The predicted viscosity obtained by the Arrhenius equation agreed satisfactorily with the experimental viscosity. The degree of fit as shown by the R^2 value was 0.99 for both salmon oil samples. As indicated above, the unrefined red and pink salmon oils were Newtonian fluids at the temperatures used in
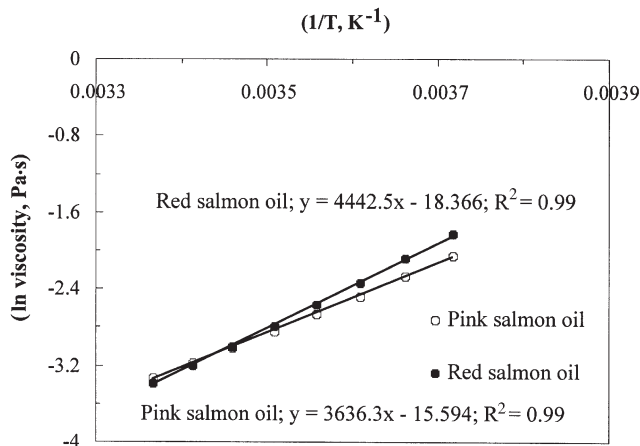

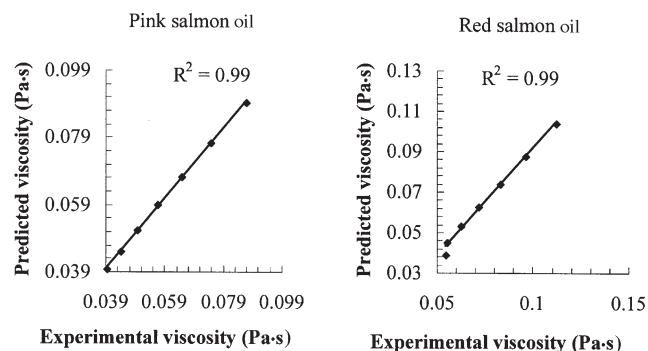**FIG. 4.** The Arrhenius plot for red and pink salmon oils.

FIG. 5. Viscosity of red and pink salmon oils predicted from the Arrhenius plot.

this study. The Arrhenius parameters found in this study are useful for predicting the viscosities of salmon oils. This study showed that the magnitude of the viscosity for salmon oils was greatly influenced at low temperatures. Each purification step of fish oil involves a different temperature condition; therefore, it is important to know how to predict the viscosity values for the salmon oils at different temperatures encountered during the processing.

ACKNOWLEDGMENTS

REFERENCES

1. Wesolowski, M., and J. Erecinska, Thermal Analysis in Quality Assessment of Rapeseed Oils, *Thermochim. Acta 323*:137–143 (1998).
2. Sathivel, S., W. Prinyawiwatkul, I.I. Negulescu, J.M. King, and B.F.A. Basnayake, Thermal Degradation of Fatty Acids and Catfish and Menhaden Oils at Different Purification Steps, *J. Am. Oil Chem. Soc. 80*:1131–1134 (2003).
3. Hassel, R.L., Thermal Analysis: An Alternative Method of Measuring Oil Stability, *J. Am. Oil Chem. Soc. 53*:179–181 (1976).
4. Gearhart, W.M., B.N. Stuckey, and J.J. Austin, Comparison of Methods for Testing the Stability of Fats and Oils, and of Foods Containing Them, *Ibid. 34*:427–430 (1957).
5. Buhri, A.B., and R.P. Singh, Thermal Properties Measurements of Fried Foods Using Differential Scanning Calorimeter, in *Developments in Food Engineering*, edited by T. Yano, R. Matsumoto, and K. Nakamura, Blackie A&P, Glasgow, 1994, pp. 201–203.
6. Kaisersberger, E., DSC Investigations of Thermal Characterization of Edible Fats and Oils, *Thermochim. Acta 151*:83–90 (1989).
7. Ritter, B., J. Schulte, and E. Schulte, Detection of Coating Waxes on Apples by Differential Scanning Calorimetry, *Eur. Food Res. Technol. 212*:603–607 (2001).
8. Iannotta, N., C. Oliviero, G.A. Ranieri, and N. Uccella, Determination of the Oil Content in Olives by the DSC Technique, *Eur. Food Res. Technol. 212*:240–243 (2001).
9. Lai, L.S., and S.J. Chao, A DSC Study on the Gel–Sol Transition of a Starch and Hsian-tsao Leaf Gum Mixed System, *J. Agric. Food Chem. 48*:3267–3274 (2000).
10. Sherman, P., *Industrial Rheology with Particular Reference to Foods, Pharmaceuticals and Cosmetics*, Academic Press, London, 1970.
11. Wiedermann, L.H., Degumming, Refining and Bleaching Soybean Oil, *J. Am. Oil Chem. Soc. 58*:159–166 (1981).
12. Sathivel, S., W. Prinyawiwatkul, I.I. Negulescu, J.M. King, and B.F.A. Basnayake, Effects of Purification Process on the Rheological Properties of Catfish Oil, *Ibid. 80*:829–832 (2003).
13. AOAC, *Official Methods of Analysis*, 16th edn., Association of Official Analytical Chemists, Arlington, VA, 1995.
14. Rao, M.A., *Rheological of Fluids and Semisolids: Principles and Applications*, An Publishers, Gaitherburg, MD, 1999.
15. SAS, *SAS/STAT User's Guide*, version 8.2, SAS Institute, Cary, NC, 2002.
16. Sathivel, S., W. Prinyawiwatkul, J.M. King, C.C. Grimm, and S. Lloyd, Oil Production from Catfish Viscera, *J. Am. Oil Chem. Soc. 80*:377–382 (2003).
17. Sathivel, S., Production, Process Design and Quality Characterization of Catfish Visceral Oil, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 2001.
18. Zhao, L., and S.H. Yalkowsky, A Combined Group Contribution and Molecular Geometry Approach for Predicting Melting Points of Aliphatic Compounds, *Ind. Eng. Chem. Res. 38*:3581–3584 (1999).
19. Ewell, R.H. The Reaction Rate Theory of Viscosity and Some of Its Applications, *J. Appl. Physics 9*:252 (1938).