Correlation of Viscosities of Vegetable Oil Blends with Selected Esters and Hydrocarbons

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ABSTRACT: Blending is often used to reduce the viscosity of vegetable oil lubricants. Experimental rheological results were compared with traditional blending charts and calculation methods. Kinematic viscosities of 90% oleic sunflower, canola, and soybean oils blended with adipates, oleates, polyalphaolefins, and mineral oil were determined at 40°C using capillary viscometers. Blending charts related the viscosities to blend composition with 5% inaccuracy compared with more than 10% deviation made by the cubic equation of Kendall and Monroe. Even more accurate and simpler correlations could be derived. A semilog relationship between viscosities and composition was more accurate than a cubic model. Higher accuracy was also achieved when relating viscosities to volume fractions rather than to weight or mole fractions. Mineral oil blends did not follow the observed rules.

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Vegetable oil (VO) is beginning to be used as a biodegradable component of lubricating base stocks. It is often problematic to calculate the amount of VO that is required to obtain a blend of a required viscosity grade, because investigations predicting the viscosities of VO blends with other biodegradable base stocks or mineral oils have not yet been reported. Polyalphaolefins of low M.W., adipates, and oleates are among the most widespread synthetic biodegradable base stocks (1–3). They are often used to reduce viscosity in VO lubricants, especially when ISO VG 22 grade is desired. Several methodologies exist to relate blend viscosities to the amounts of the components; however, it is unclear whether viscometric properties of VO can be considered sufficiently similar to those of mineral oils or lubricating base stocks in general. Although TAG (major components of VO) are chemically quite similar to synthetic esters, they contain *cis*-unsaturation, which is not found in other lubricating base stocks (4,5). Their M.W. are much higher than those of mineral oils, polyalphaolefins, or synthetic esters. Therefore, it can be expected that viscometric properties of VO can be somewhat unusual compared with those of typical lubricating base stocks.

Traditionally, blending charts and blending indices (BCBI) are used to predict viscosities when petroleum fractions are blended (6,7). In this procedure, as shown in Equation 1, blending indices, BI_i, are first established for each component from a typical blending chart (based on their original viscosities, v_i) (see Fig. 1 and Ref. 8):

$$\mathrm{BI}_i = f(v_i) \qquad [1]$$

Similarly, in Equation 2, the procedure shows that a cumulative blending index, $\mathrm{BI}_{\mathrm{blend}}$, can be calculated assuming that the blending index is an additive property on volume basis:

$$\mathrm{BI}_{\mathrm{blend}} = \Sigma\, \mathrm{BI}_i \times \mathrm{vol}_i = \mathrm{BI}_1 \times \mathrm{vol}_1 + \mathrm{BI}_2 \times \mathrm{vol}_2 + \cdots + \mathrm{BI}_n \times \mathrm{vol}_n \qquad [2]$$

where vol_i is the volume fraction of component i, 0.0 to 1.0.

In the last step (Eq. 3), the procedure states that the blend viscosity v_{blend} is obtained from the same blending chart (Fig. 1) by matching it to the cumulative blending index:

$$v_{\mathrm{blend}} = f\,(\mathrm{BI}_{\mathrm{blend}}) \qquad [3]$$

It is not clear whether this methodology can be successfully extended to VO, synthetic esters, and other biodegradable base stocks. It has been recognized (9) that there are no firm theories to relate blend viscosity to the properties of pure components. Because viscosities can be affected by an interaction between components, the blend viscosity also depends on binary parameters. The most general correlations, which

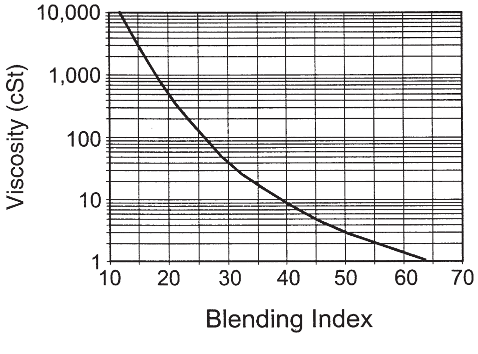

FIG. 1. Blending chart used in this investigation, adapted from Reference 8.

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do not account for binary interactions, are the cubic equation by Kendall and Monroe (K&M) (9–11) and a semilog equation by Irving (9,12,13). The K&M equation considers that the cubic root of dynamic viscosity can be assumed an additive property on a molar basis (Eq. 4):

$$v_{\text{blend}} \times \rho_{\text{blend}} = \mu_{\text{blend}} = [3\chi_i \times \sqrt[3]{\mu_i}]^3$$
$$= [\chi_1 \times \sqrt[3]{\mu_1} + \chi_2 \times \sqrt[3]{\mu_2} + \cdots + \chi_n \times \sqrt[3]{\mu_n}]^3 \qquad [4]$$

where v_{blend} is kinematic viscosity, mm^2/s; μ_{blend} is dynamic viscosity, Pa·s; ρ is density, kg/m^3; and χ is molar fraction, 0.0 to 1.0.

The Irving correlation considers that the natural logarithm of kinematic viscosity $<_i$ can be assumed an additive property on a weight basis (Eq. 5):

$$\ln v_{\text{blend}} = \Sigma\, m_i \times \ln v_i = m_1 \times \ln v_1 + m_2 \times \ln v_2 + \cdots + m_n \times \ln v_n \qquad [5]$$

where m_i is the weight fraction of component *i*, 0.0 to 1.0.

Equation 5 can also be rewritten as appears in Equation 6:

$$v_{\text{blend}} = \pi\, v_i^{m_i} = v_1^{m1} \times v_2^{m2} \times \cdots \times v_n^{m_n} \qquad [6]$$

For more accurate predictions, the correlations that account for binary interactions were used. The MacAllister correlation has been reported applicable for aromatic oils (14) and TG blends (15). For binary mixtures it can be expressed as shown in Equation 7:

$$\ln v_{\text{blend}} = \chi_1^3 \ln v_1 + 3\,\chi_1^2\,(1 - \chi_1) \ln v_{12}$$
$$+ 3\chi_1\,(1 - \chi_1)^2 \ln v_{21} + (1 - \chi_1)^3 \ln v_2 + r^0 \qquad [7]$$

where v_{12} and v_{21} are viscosities of the mixture (which need to be established from experimental data) and r^0 is the correction factor for M.W. (14,15).

However, the binary parameters may vary significantly with different oils and blend components. Use of such correlations for blends of undefined composition is somewhat limited, especially when VO themselves represent mixed acid TG with possible binary interactions. In this study only BCBI, K&M, and Irving correlations were used, including several of their modified forms.

The current investigation deals with viscometrics of blends with VO used for lubricant applications, such as canola oil (16), high-oleic sunflower oil (HOSO) (17), and soybean oil (18). Mineral oil was tested to observe if it also followed the viscosity/blending relationships established for the abovementioned fluids.

MATERIALS AND METHODS

The blending mixtures were prepared by weight using an analytical balance with a precision of ±0.1 mg. The mixtures were then stirred at room temperature for 30 min to prepare the final blend. Kinematic viscosity was measured according to ASTM D Method 445 using a Cannon–Fenske capillary viscometer (State College, PA). Viscometers were calibrated with standard fluids supplied by the manufacturer within ±0.3% by making at least four independent measurements for each of three viscometers. Samples were thermally equilibrated for at least 30 min before each determination at 40 ± 0.2°C. Although such temperature fluctuation translated into another ±0.2% deviation in viscosity, the total deviations did not exceed ±0.5%. Viscosities of the calibration fluids were determined using at least three different viscometers and were in agreement with the values supplied by fluid manufacturers.

Alkali-refined canola and soybean oils (refined, bleached, deodorized, winterized) represented commercial food-grade products. Soybean oil (Pioneer Hi-Bred International, Inc., Des Moines, IA) contained 16% palmitic/stearic, 23% oleic, 53% linoleic, and 8% linolenic acids and a tocopherol level of approximately 500 ppm. Canola oil (obtained from a local grocery store) contained 3% palmitic/stearic, 60% oleic, 30% linoleic, and 7% linolenic acids, and approximately 1000 ppm tocopherol. A genetically modified HOSO (International Flora Tech Ltd., Gilbert, AZ) had 5% palmitic/stearic, 90% oleic, and 5% linoleic/linolenic acids, and approximately 1000 ppm tocopherol.

Isobutyl oleate (i-Bu oleate) (Aldrich Chemical, Milwaukee, WI) contained 7% polyunsaturated esters as contamination and had a M.W. of 339 g/mol and a density of 0.853 g/cm^3 at 40°C. All oleates and oils were stored below +5°C under nitrogen atmosphere before the experiments. Polyalphaolefins PAO 2 and PAO 4 (Amoco Chemicals, Lisle, IL) essentially represented 90:10 and 80:20 mixtures of hydrogenated dimers and trimers of 1-decene with average M.W. of 287 and 437 g/mol and densities of 0.778 and 0.798 g/cm^3 at 40°C, respectively. Additive-free "white" super-refined mineral oil (SRMO) with a low sulfur content had a boiling range of 360–530°C and met Military Specification for Lubrication Products no. 7828. Its density at 40°C was 0.81 g/cm^3 and average M.W. was 325 g/mol. Isotridecyl adipate (i-C_{13} adipate) (Aldrich Chemical) contained negligible amounts of minor constituents and had a M.W. of 511 g/mol and a density of 0.895 g/cm^3 at 40°C.

RESULTS AND DISCUSSION

Multiple viscosity measurements were obtained for each blend component, and average kinematic viscosities are reported in Table 1. The VO fluids were blended with PAO 4 and i-C_{13} adipate at ratios of 90:10, 75:25, 50:50, and 25:75 (w/w). Viscosities of these blends were measured, and their dependence on diluent concentration is shown in Figure 2. As expected, viscosity decreased with higher amounts of diluent. However, the decrease was not linear. The experimental values are compared with those predicted by Irving, K&M, and BCBI correlations in Table 3. One can observe that the K&M equation deviates from the experimental data much more than the other two correlations. This can also be observed in Figure 3 where additional data points are incorporated for soybean oil blended with PAO 4.

TABLE 1
Kinematic Viscosities of Original Components Used for Blending[a]

Vegetable oils	cSt	Diluents	cSt	Comparison oils	cSt
HOSO	40.25	i-C_{13} adipate	27.25	SRMO	71.2
Soybean	31.60	PAO 4	17.45	i-Bu oleate	6.20
Canola	38.05			PAO 2	5.45

[a] Cannon–Fenske capillary viscometers, ASTM Method D 445, cSt at 40°C. SRMO, super-refined mineral oil; PAO, polyalphaolefin; i-Bu oleate, isobutyl oleate; HOSO, high-oleic sunflower oil; i-C_{13} adipate, isotridecyl adipate.

BCBI shows a good match with the experimental data in Figure 3; however, its predictions are not always better than those of the Irving equation. This raises questions as to which type of fraction (weight, volume, or mole) and which type of dependence (semilog or cubic) is more appropriate for use in the correlation. To find an answer, the mean deviation can be calculated by arithmetically averaging the moduli of all percentage deviations made by a particular correlation. Their comparison would then demonstrate which correlation makes the smallest deviations.

Correlations can also be modified to simplify them or improve their accuracy. In essence, volume fractions can also be used, as can kinematic viscosities (rather than dynamic in K&M). Generally, if visc denotes dynamic or kinematic viscosities and fr denotes weight, volume, or mole fractions, each semilog correlation can be expressed as shown in Equation 8:

$$\ln \text{visc}_{\text{blend}} = \Sigma\, \text{fr}_i \times \ln \text{visc}_i \qquad [8]$$

and each cubic correlation as in Equation 9:

$$\text{visc}_{\text{blend}} = (\Sigma\, \text{fr}_i \times \sqrt[3]{\text{visc}_i})^3 \qquad [9]$$

Because very few studies have been done to establish the most suitable correlations, all possible correlations utilizing both cubic and semilog relationships, both kinematic and dynamic viscosities, and all three types of fractions (weight, volume, and mole) were applied to predict the data listed in Table 2. The mean aggregate errors were calculated and compared as shown in Figure 4 and listed in Table 3.

None of the three correlations (Irving, K&M, and BCBI) was in agreement with the fact that the least aggregate error is produced when the prediction employs a semilog relationship between dynamic viscosities and volume fractions. Also,

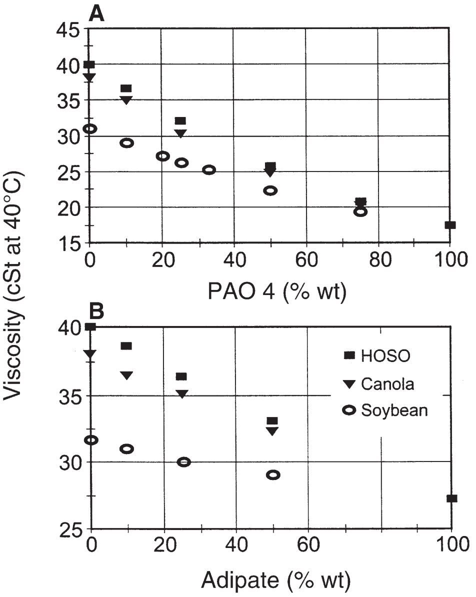

FIG. 2. (A) Decrease in kinematic viscosities of vegetable oil blends vs. dilution with polyalphaolefin (PAO) 4; (B) decrease in kinematic viscosities vs. dilution with isotridecyl adipate. HOSO, high-oleic sunflower oil.

TABLE 2
Viscosities of Vegetable Oil Blends (w/w) with PAO 4 and Adipate; Determination of Prediction Errors Made by Irving, Kendall and Monroe, and Blending Chart/Blending Index Correlations[a]

Blend	HOSO				Canola				Soybean			
VO/diluent	cSt	%[b]	%[c]	%[d]	cSt	%[b]	%[c]	%[d]	cSt	%[b]	%[c]	%[d]
Neat VO, 100:0	40.25				38.05				31.6			
PAO 4, 90:10	36.50	2.3	−7.1	−0.6	34.92	1.3	−8.2	−1.5	29.13	4.6	−5.4	2.2
PAO 4, 75:25	32.17	2.2	−13.1	−3.0	30.33	4.7	−10.8	−0.2	26.23	7.1	−9.6	2.8
PAO 4, 50:50	25.70	3.5	−10.6	−1.8	24.82	4.6	−10.0	−0.5	22.48	7.1	−9.3	2.4
PAO 4, 25:75	20.74	3.4	−4.4	0.3	20.38	4.0	−4.1	1.0	19.70	3.8	−5.6	0.9
i-C_{13} adipate, 90:10	38.65	0.5	−5.7	−0.0	36.51	2.7	−3.5	2.3	31.02	2.7	−3.5	2.5
i-C_{13} adipate, 75:25	36.44	0.5	−10.5	−0.4	35.15	−1.3	−12.4	−2.1	30.15	7.0	−4.5	6.7
i-C_{13} adipate, 50:50	33.14	−0.2	−11.8	−1.3	32.31	−1.0	−12.9	−2.0	29.06	6.6	−6.2	6.2

[a] VO, vegetable oil; see Table 1 for other abbreviations.
[b] % Deviation made by prediction of the Irving equation.
[c] % Deviation made by prediction of the Kendall and Monroe equation.
[d] % Deviation made by prediction of the blending chart/blending index correlation.

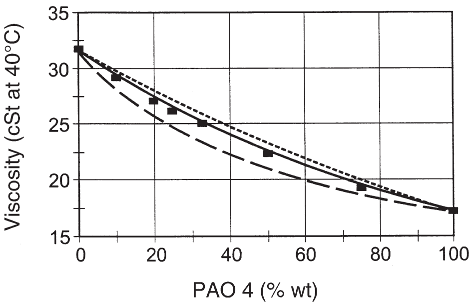

FIG. 3. Predicted kinematic viscosities of soybean oil blended with PAO 4 (■). Irving prediction (----), blending chart prediction (—), Kendall and Monroe prediction (– – –). For abbreviation, see Figure 2.

TABLE 3
Mean Aggregate Errors (%) for Predictions Based on Equations 8 and 9 for the Data in Table 3

	Kinematic		Dynamic	
Fraction	Semilog	Cubic	Semilog	Cubic
Weight	3.38[a]	5.19	3.62	5.60
Volume	2.37	3.77	2.14	3.93
Mole	9.48	7.72	11.02	8.06[b]

[a] Represents the Irving equation.
[b] Represents the Kendall and Monroe equation.

the two semilog relationships based on volume fractions showed better predictions than BCBI, Irving, or K&M correlations. It can be suggested that volume fractions are more suitable for viscosity prediction than weight or mole fractions and that the semilog relation is more suitable than the cubic relation. However, more experimental investigations are needed to strengthen these suppositions. No appropriate experimental data by other investigators have been found to verify the above correlations for VO, and it has been pointed out (14) that very few data are available on TAG blends.

To extend the above observations to more fluids, i-Bu oleate and PAO 2 were blended with VO, as shown in Table 4. Viscosities of these fluids also seemed to fall into the same range of predictions, but quantitative conclusions can be drawn only after more extensive testing.

Because only four diluents were used in this investigation, it is not clear whether the conclusions can be applied to all biodegradable fluids. With blends of HOSO and SRMO it has been demonstrated (19) that actual viscosities may show large deviations from the above correlations (Fig. 5). Mineral oil, such as SRMO, being very different in structure from the above biodegradable fluids, may enter into various interactions with blending components, thus affecting the blend viscosity. Likewise, unconventional VO, such as castor, meadowfoam, lesquerella, or jojoba oils, may not follow the above rules either, because their structural properties are significantly different from a typical VO.

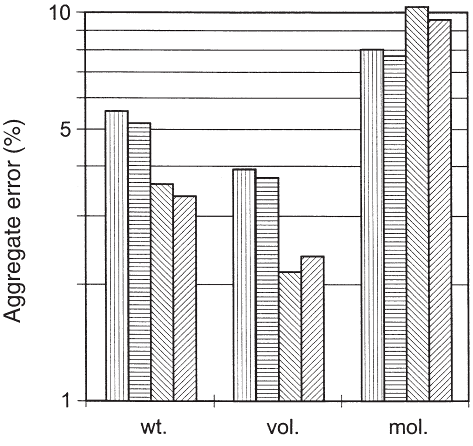

FIG. 4. Mean aggregate errors (%) made by correlations based on cubic and semilog relations of kinematic and dynamic viscosities to volume, weight, and mole fractions (see Eqs. 9 and 10; data from Table 3). Dynamic viscosity–cubic relationship (bars with vertical lines); kinematic viscosity–cubic relationship (bars with horizontal lines); dynamic viscosity–semilog relationship (bars with lines slanting up, left to right); kinematic viscosity–semilog relationship (bars with lines slanting down, left to right).

It is not clear to which temperature range the listed correlations would be most applicable. The current investigation deals only with viscosities at 40°C. At higher temperatures chemical interactions may become more pronounced, which in turn may affect the blend viscosity. At lower temperatures the possibility of formation of structured segments by TAG increases (20), which may contribute to the viscosity. Minor changes in viscosity with very low dilution were not tested either, because the lowest investigated dilution was 10% wt. Therefore, more experimental studies are needed to expand the applicability of the above methodology.

The following conclusions may be drawn: (i) Viscosity of vegetable oil blends with oleates, PAO, and adipates at 40°C may be predicted with about 5% inaccuracy using blending charts; (ii) larger deviations were observed when relating viscosities to mole fractions than to weight or volume fractions; (iii) the correlations may not be extended to mineral oils without compromising accuracy.

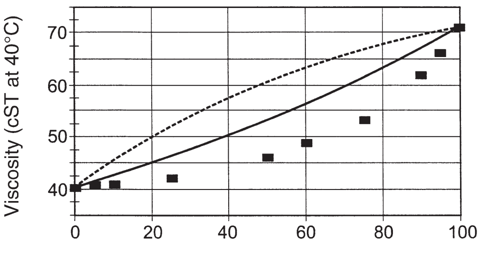

FIG. 5. Kinematic viscosities (■) of HOSO blends with super-refined mineral oil (SRMO). Predictions of blending chart and Irving equation (—) and Kendall and Monroe correlation (----). For other abbreviation, see Figure 2.

TABLE 4
Viscosities and Percentage Deviations of VO Blends (w/w) with PAO 2 and Oleate[a]

		HOSO				Soybean oil			
Diluent	Diluent/VO	cSt	%[b]	%[c]	%[d]	cSt	%[b]	%[c]	%[d]
i-Bu oleate	20:80	27.2	–1.5	16.0	8.5	23.5	2.9	20.8	10.1
i-Bu oleate	50:50					14.1	0.3	13.9	7.9
PAO 2	20:80					21.6	–2.8	19.9	7.6
PAO 2	40:60	26.2	–4.5	13.0	5.5				

[a] See Tables 1 and 2 for abbreviations.
[b] % Deviation made by prediction of the Irving equation.
[c] % Deviation made by prediction of the Kendall and Monroe equation.
[d] % Deviation made by prediction of the blending chart/blending index correlation.

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REFERENCES

1. Carpenter, J.F., Biodegradability and Toxicity of Polyalphaolefin Base Stocks, *J. Synth. Lubr. 12*:13–20 (1995).
2. Van der Waal, G., and D. Kenbeek, Testing, Application and Future Developments of Environmentally Friendly Ester Base Fluids, *Ibid. 10*:67–83 (1993).
3. Shubkin, R.L., Polyalphaolefins, in *Synthetic Lubricants and High Performance Functional Fluids*, edited by R.L. Shubkin, Marcel Dekker, New York, 1993, pp. 9–11.
4. Lawate, S.S., K. Lal, and C. Huang, Vegetable Oils—Structure and Performance, in *Tribology Data Handbook*, edited by E.R. Booser, CRC Press, Boca Raton, 1997, pp. 103–116.
5. Mang, T., Lubricants, in *Lipid Technologies and Applications*, edited by F.D. Gunstone, and F.B. Padley, Marcel Dekker, New York, 1997, pp. 737–758.
6. Gary, J.H., and G.E. Handwerk, *Petroleum Refining: Technology and Economics*, Marcel Dekker, New York, 1994.
7. Jones, D.S.J., *Elements of Petroleum Processing*, John Wiley & Sons, New York, 1995.
8. Maxwell, J.B., *Data Book on Hydrocarbons; Application to Process Engineering*, Van Nostrand, New York, 1950.
9. Green, D.W., and J.O. Maloney, *Perry's Chemical Engineers' Handbook*, 7th edn., McGraw-Hill, New York, 1997, pp. 3–251.
10. Kendall, J., and K.P. Monroe, The Viscosity of Liquids. II. The Viscosity–Composition Curve for Ideal Liquid Mixtures, *J. Am. Chem. Soc. 39*:9, 1787–1806 (1917).
11. Eiteman, M.A., and J.W. Goodrum, Density and Viscosity of Low-Molecular Weight Triglycerides and Their Mixtures, *J. Am. Oil Chem. Soc. 71*:1261–1265 (1994).
12. Irving, J.B., Viscosities of Binary Liquid Mixtures: A Survey of Mixture Equations, NEL Report No. 630, National Engineering Laboratory, Glasgow, United Kingdom, February 1977.
13. Irving, J.B., Viscosities of Binary Liquid Mixtures: The Effectiveness of Mixture Equations, NEL Report No. 631, National Engineering Laboratory, Glasgow, United Kingdom, February 1977.
14. Barata, P., and L. Serrano, Densities and Viscosities of Thymol + 1,8-Cineole, *J. Chem. Eng. Data 39*:298–301 (1994).
15. Valeri, D., and A.J.A. Meirelles, Viscosities of Fatty Acids, Triglycerides, and Their Binary Mixtures, *J. Am. Oil Chem. Soc. 74*:1221–1226 (1997).
16. Kassfeldt, E., and D. Goran, Environmentally Adapted Hydraulic Oils, *Wear 207*:41–45 (1997).
17. Gapinski, R.E., I.E. Joseph, and B.D. Layzell, A Vegetable Oil-Based Tractor Lubricant, *SAE Technical Paper 941758*, Society of Automotive Engineers, 1994, pp. 1–9.
18. Honary, L.A.T., Performance of Selected Vegetable Oils in ASTM Hydraulic Tests, *SAE Technical Paper 952075*, Society of Automotive Engineers, 1995, pp. 1–6.
19. Asadauskas, S., and S.Z. Erhan, Prediction of Viscosities of Hydrophobic Carriers Produced by Blending Biodegradable Ester Based Fluids, in *Proceedings of the 28th Annual Meeting*, Fine Particle Society, Dallas, 1998, pp. 1–2.
20. Larsson, K., and P. Dejmek, Crystal and Liquid Crystal Structures of Lipids, in *Food Emulsions*, edited by K. Larsson and S.E. Friberg, Marcel Dekker, New York, 1990, p. 109.

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