Inter-relationships Among the Properties of Fatty Oils

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Properties of fatty oils, such as viscosity (η), iodine value (IV) and saponification value (SV), are useful in the design of methods and equipments for the processing of the fatty oils to value-added products. This investigation is aimed at the development of generalized empirical relationships based on a model similar to the Antoine equation for vapor pressure. Two equations resulted. The first equation:

$$\log \eta = [-1.4 + 1.25\,(IV/SV)] + [500 - 375(IV/SV)]/[(t + 140) - 85(IV/SV)]$$

relating the logarithm of viscosity to the ratio of iodine value to saponification value (IV/SV) and temperature in degrees centigrade (t), gives an average absolute deviation of 13.0% at 77 data points of several fatty oils. The second equation, somewhat simpler in form:

$$\log \eta = -0.6298 + [273.66/(t + 88.81)]$$

relating the logarithm of viscosity directly to the temperature in degrees centigrade (t), gives an average absolute deviation of 14.5% at 89 data points of a larger group of fatty oils ranging from almond to tallow.

The two equations can be used conveniently to predict either viscosity, iodine value or saponification value, when the other two properties are known, for design purposes.

The utility of fatty oils as constituents in food products, surface coating formulations, pharmaceuticals and cosmetics has been well known for a long time. To design and operate the associated unit processes and unit operations in different industries (which use the fatty oils), knowledge of at least a few physical properties is essential. Among the transport properties, viscosity (which is a measure of internal friction of the molecules) is the most important, from the point of design and process control. During polymerization and hydrogenation, the viscosity of oils increases. Changes in viscosity in such processes can be used to monitor the process, e.g., stop the polymerization or hydrogenation, at the required level. Viscosity is also influenced by changes in temperature, generally decreasing exponentially with increase in temperature.

Viscosity - temperature (η-t) relationships are of good value in programming the process control of the units for important reactions such as hydrogenation and polymerization. A careful literature survey revealed that, in spite of its importance for design and process control purposes, only Haighton and coworkers (1) studied the problem and tabulated the constants "a" and "b" of the model

$$\log \eta = a + 10^6 b\, T^{-3} \qquad [1]$$

for 16 oils. The values of "a" and "b" tabulated by the investigators (1) for each fatty oil can be used in conjunction with equation [1] to calculate the viscosity from the absolute temperature (T) in degrees kelvin, with an average absolute deviation of 3.2%. With the availability of more data in the compilations of Lange (2), Bailey (3) and the CRC Handbook (4), it was desirable to attempt further work on the η-t relationships, with the twin objectives of (a) exploring the possibility of proposing interrelationships between important properties characterizing fatty oils, and (b) developing a reasonably simple η-t relationship applicable to fatty oils.

TREATMENT OF EXPERIMENTAL DATA

The η-t data available in the literature (1-4) are converted by suitable calculations (such as multiplication by density when the reported values are kinematic viscosities) to arrive at the tables of dynamic viscosities in centipoise (η) as a function of temperature (t) in degrees centigrade for all 26 oils mentioned in Table 1. Density in g/ml at any temperature (t) is calculated, wherever necessary, from the density at 20°C following Bailey's recommendation:

$$\rho_t = \rho_{20} - 0.00064\,(t-20) \qquad [2]$$

Recent evaluations (5) showed that the Antoine model represents the vapor pressure of liquids better than the Andrade model. In view of certain theoretical and practical considerations, which can be centered around the exponential change in both vapor pressure and viscosity with temperature, the same models have often been used to represent the two properties. The Antoine model has been used, as an optimal choice between simplification and practical utility, to represent the η - t relationships for the present study. By means of least-squares analysis, the absolute viscosity (η) vs temperature (t) data of each fatty oil are fitted to the Antoine model:

$$\log \eta = A^1 + B^1/(t+C^1) \qquad [3]$$

The behaviors of the set of coefficients A^1, B^1 and C^1 of the fatty oils are investigated to evolve any relationships with other characteristic properties, and the possibilities of arriving at a generalized equation for the viscosity of all the fatty oils.

It is customary for oil technologists to measure the IV and SV to ascertain the degree of unsaturation and molecular chain length. From a practical standpoint, it is desirable to investigate the possibilities of relating a transport property needed in design work, such as viscosity, to the characteristic properties such as the IV and SV, rather than develop and suggest additional measurements for the purpose of estimating viscosity. A careful examination of the literature data (2-4) shows the following trends in the behavior of fatty oils:

(a) Viscosity slightly decreases with increase in the unsaturation measured in terms of the IV.
(b) Viscosity slightly increases with molecular weight (for oils containing fatty acids) qualitatively described by the SV.

In view of the small opposing influences of the two factors, the second being selective, the ratio of IV to SV is

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TABLE 1

Comparison of Predicted Viscosity with Experimental Data

Fatty Oil	Range of temp. (°C)	No. of data points	Range of observed viscosity, cP	Range of calculated viscosity, cP (Eqn. [4])	% Deviation		Range of calculated viscosity, cP (Eq. [7])	% Deviation	
					Av Abs	Max		Av. Abs.	Max.
1	2	3	4	5	6	7	8	9	10
Almond	37.8- 98.9	2	39.20- 7.59	34.16- 6.55	13.27	-13.68	34.00- 6.73	12.28	-13.23
Butter fat	40.0- 60.0	2	34.00-17.00	27.92-14.52	16.24	+17.89	31.24-16.20	6.46	+ 8.13
Coconut	37.8- 98.9	4	27.15- 5.29	26.83- 5.10	5.01	+ 8.25	34.00- 6.73	20.94	-27.23
Cod liver	37.8- 98.9	2	29.59- 6.73	24.28- 5.66	16.79	+17.96	34.00- 6.73	7.47	-14.93
Corn	20.0- 60.0	3	70.00-16.00	74.17-15.60	2.95	- 5.96	76.76-16.20	4.98	- 9.66
Cottonseed	20.0- 98.9	3	70.40- 7.28	76.21- 6.55	7.44	+10.03	76.76- 6.73	7.01	- 9.04
Groundnut	20.0- 60.0	3	82.00-19.00	76.67-16.22	10.80	+14.64	76.76-16.20	11.09	+14.81
Cottonseed[a]	40.0- 60.0	2	45.00-23.00	-	-	-	31.24-16.20	30.10	+30.59
Rapeseed[a]	40.0- 60.0	2	49.00-24.00	-	-	-	31.24-16.20	34.40	+36.25
Soybean[a]	40.0- 60.0	2	33.00-18.00	-	-	-	31.24-16.20	7.70	+10.08
Lard	37.8- 98.9	4	40.08- 7.61	33.19- 6.20	17.01	+18.50	34.01- 6.73	13.68	+15.15
Lardolein	40.0- 60.0	2	36.00-18.00	-	-	-	31.24-16.20	11.66	+13.23
Linseed	30.0- 98.9	5	33.10- 6.45	27.28- 5.17	20.62	+25.94	47.15- 6.73	21.74	-42.44
Neatsfoot	37.8- 98.9	2	39.03- 7.36	33.90- 6.35	13.39	+13.69	34.01- 6.73	10.70	+12.87
Mustard	37.8- 98.9	2	41.18- 8.26	33.71- 6.55	19.45	+20.75	34.01- 6.73	17.96	+19.41
Olive	10.0-100.0	13	138.0 - 7.00	133.4- 6.36	8.63	+18.58	137.9 - 6.6	8.24	+19.40
Palm	40.0- 60.0	2	37.00-19.00	29.72-15.37	19.40	+19.67	31.24-16.20	15.20	+15.58
Palm kernel	37.8- 98.9	2	28.07- 5.65	27.87- 5.27	3.70	+ 6.69	34.01- 6.73	20.14	-21.15
Palm olein	40.0- 60.0	2	37.00-19.00	-	-	-	31.24-16.20	15.20	+15.58
Rapeseed	15.6-100.0	9	111.8 - 8.00	95.72- 6.39	22.62	+27.13	97.98- 6.60	20.57	+25.,39
Raw perilla	37.8- 98.9	2	23.18- 6.02	14.56- 4.43	31.83	+37.20	34.01- 6.73	29.25	-46.71
Refined whale	37.8- 98.9	2	28.68- 6.50	31.85- 6.42	6.28	-11.04	34.01- 6.73	10.90	-18.58
Sardine	37.8- 98.9	2	25.83- 6.27	20.07- 5.16	19.99	+22.30	34.01- 6.73	19.50	-31.66
Soybean	20.0- 98.9	8	60.00- 6.63	70.21- 6.35	7.01	-19.22	76.76- 6.73	13.07	-30.95
Sunflower	20.0- 98.9	5	63.00- 6.68	69.11- 6.17	5.94	- 9.69	76.76- 6.73	8.74	-21.85
Tallow	65.7-100.0	2	17.68- 7.80	12.75- 5.75	26.95	+27.55	13.85- 6.60	18.36	+21.33
Overall	10 -100	89	138.0 - 5.29	133.4 - 5.10	13.0		137.9 - 6.20	14.5	

[a]Hydrogenated.

chosen to be relatable to the transport property-viscosity. The set of coefficients A^1, B^1, and C^1 are related to the ratio (IV/SV). The coefficients also have been averaged giving due weight to the different classes of the fatty oils studied.

RESULTS AND DISCUSSION

Efforts to relate the coefficients of the Antoine type equation to the ratio (IV/SV) finally gave rise to the following equation for viscosity:

$$\log \eta = (-1.4 + 1.25(IV/SV) + [500 - 375(IV/SV)]/[(t + 140) - 85(IV/SV)] \quad [4]$$

The details of the prediction capabilities of equation [4] at 77 data points of 21 fatty oils are summarized in Table 1. Deviations are calculated from:

$$\% \text{ deviation} = d = \frac{\eta_{obs} - \eta_{cal}}{\eta_{obs}} \times 100 \quad [5]$$

$$\% \text{ average absolute deviation} = \bar{d} = \frac{|d|}{N} \quad [6]$$

where η_{obs} is the observed viscosity, η_{cal} is the calculated viscosity and $|d|$ is the sum of the magnitudes of the deviations for N data points. Equation [4], which predicts the viscosity for the above set with an average absolute deviation of 13% can be used to estimate viscosity of fatty oils. Alternately, if viscosity data are available, either IV or SV can be estimated from a knowledge of the other property.

The generalized relation for viscosity developed from carefully weighted coefficients of the Antoine type equation is

$$\log \eta = -0.6298 + [273.66/(t + 88.81)] \quad [7]$$

As shown in Table 1, equation [7] represents the viscosity of 26 fatty oils at 89. points estimated according to equations [5] and [6] with an average absolute deviation of 14.5%

A careful analysis of the results presented in Table 1 shows that the substances represent a good cross section of fatty oils in terms of utility and properties; wide ranges of temperature (0-100°C) and viscosity (5-138 cP) are represented, and the prediction capabilities of the relationships proposed are commensurate with the accuracies required in the design estimates for liquid viscosity. Equations [4] and [7] are therefore recommended in the absence of experimental data.

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