Effect of Hydrogenation on Density and Viscosity of Sunflowerseed Oil

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ABSTRACT: The densities and viscosities of unhydrogenated and hydrogenated sunflowerseed oils have been determined at temperatures ranging from 25 to 50°C at 5°C intervals. The densities of these oils vary linearly with temperature. The values of the parameters for the density equation have been calculated. Smooth curves were obtained when the changes in viscosity with temperature were plotted in the form of ln η vs. $1/T$. The energy of activation, the free energy of activation, and the entropy of activation have been calculated at 25°C, and they decreased with the degree of unsaturation in the fatty acid chains of the sunflowerseed oil.
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KEY WORDS: Activation energy, activation entropy, activation free energy, density, hydrogenation, sunflowerseed oil, viscosity.

Because viscosity is an important physicochemical property, many investigators have determined the densities and viscosities of the methyl esters of *n*-alkanoic acids (1–4). Liew *et al.* (5) determined the densities and viscosities of the methyl esters of hexanoic, heptanoic, octanoic, decanoic, and dodecanoic acids at temperatures from 10 to 80°C. The densities of these esters vary linearly with temperature. Smooth curves were obtained when the fluidities were plotted against molal volumes of esters. Kapseu *et al.* (6) have determined the viscosity of cottonseed oil to facilitate the fractionation of refined cottonseed oil.

Hydrogenation of oils and fats is the largest single chemical reaction in the fatty oil processing industry. Simply stated, hydrogenation is the addition of hydrogen to the ethylenic linkages or double bonds by reaction with hydrogen in the presence of a metal catalyst. Vegetable oils are mixed triglycerides of saturated fatty acids, such as myristic, palmitic, and stearic; and unsaturated fatty acids that contain one, two, three, or more unsaturated bonds in each fatty acid, such as oleic, linoleic, and linolenic. Because each double bond may be isomerized or hydrogenated at different rates, depending on its position or environment in the molecule, the hydrogenation reaction is quite complex (7,8). Another important factor is that the position of a fatty acid on the glycerol determines the physical properties of the molecule.

Morrison and Robertson (9) have determined the viscosities of heated hydrogenated and unhydrogenated sunflowerseed oils to show the effects of hydrogenation on the stability of the oils.

In the present study, we have determined the densities and viscosities of unhydrogenated and hydrogenated sunflowerseed oils at temperatures from 25 to 50°C. Our study was aimed at demonstrating structural changes in unhydrogenated and hydrogenated oils.

EXPERIMENTAL PROCEDURES

The samples used in this work, refined and bleached unhydrogenated and hydrogenated oils, were supplied by the Trakya Birlik (Thrace Union) Company (Edirne, Turkey).

Hydrogenation was carried out under the following conditions: catalyst concentration, 0.02% as nickel; temperature, 180°C; pressure, 2 atm H_2; agitation, 450 rpm; and reaction time, 25 min.

For analysis of the fatty acid composition, a Shimadzu GC 6 AM Model gas chromatograph was used (Shimadzu, Kyoto, Japan). The type of gas chromatographic column was 2 m × 1/4″ × 2 mm glass, packed with 5% PEGA on chromosorb W 60–80 mesh, and its conditions were: injector temperature, 225°C; detector temperature, 225°C; column temperature, 175°C; gas pressure, air, 1 kg cm^{-2}; gas pressure, H_2, 3 kg cm^{-2}; carrier gas pressure, 5 kg cm^{-2}; and sample quantity, 1 μL of 3% solution in hexane.

Because the time of flow is high, the Ostwald procedure is not suitable for determination of the viscosity of highly or moderately viscous liquids at 25°C. For this purpose, the falling-ball viscometer (10), Haake Type B 3 Veb MLW (Medingen, Germany), was used. This consists in determining the time necessary for a small ball of known density to fall through a fixed distance in a column of a reference liquid and in the liquid whose viscosity we wish to measure. A chrome–steel ball with a diameter of 7.5 mm was used for this purpose. Water can be used as a reference liquid (11). The viscometer was carefully cleaned, rinsed with distilled water and ethanol, and dried before it was filled with an oil sample. The error in the flow time was 0.01 s.

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The formula used for the determination of viscosity was as follows:

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad [1]$$

where d is density and t is the falling time of the ball. If substance 2 is the reference liquid, water, w, we can use the following equation:

$$\frac{\eta}{\eta_w} = \frac{dt}{d_w t_w} \quad [2]$$

Hence, it becomes:

$$\eta = \frac{\eta_w}{d_w t_w} dt = kdt \quad [3]$$

where k is equal to $\eta_w / d_w t_w$.

Density was determined with a 10-mL pycnometer, and the error of measurement was within ±0.0001 g mL^{-1}. The iodine values were determined by the Wijs method (12).

RESULTS AND DISCUSSION

The fatty acid compositions of unhydrogenated and hydrogenated sunflowerseed oil are shown in Table 1. The contents of myristic, palmitic, and stearic acids, which have no double bond, do not change appreciably, whereas the linoleic acid content is decreased from 63.9 to 9.7% by hydrogenation, and oleic acid is increased from 24.7 to 76.6%. Therefore, the presence of the unsaturated fatty acids (linoleic and oleic) in the oil proves that the hydrogenation was not completed (Table 1). As mentioned previously, each double bond may be isomerized or hydrogenated at different rates, depending on its position or environment in the molecule.

The determined iodine value is decreased from 131.7 to 82.4. Thus, unhydrogenated oil has more unsaturation than hydrogenated oil and is liquid, whereas hydrogenated oil is solid at room temperature.The densities and viscosities of unhydrogenated and hydrogenated sunflowerseed oils are tabulated in Table 2. The accuracy of the density data was further evaluated by correlating them with temperature (K) by means of:

$$d = k + l\,T\,(\mathrm{K}) \quad [4]$$

TABLE 1
Fatty Acid Compositions (wt%) and Iodine Values of Unhydrogenated and Hydrogenated Sunflowerseed Oils

Fatty acid	Unhydrogenated	Hydrogenated
Myristic ($C_{14:0}$)	0.1	0.1
Palmitic ($C_{16:0}$)	7.7	8.5
Stearic ($C_{18:0}$)	3.6	5.1
Oleic ($C_{18:1}$)	24.7	76.6
Linoleic ($C_{18:2}$)	63.9	9.7
Iodine value	131.7	82.4

TABLE 2
Densities and Viscosities of Unhydrogenated and Hydrogenated Sunflowerseed Oils[a]

		Unhydrogenated		Hydrogenated	
t (°C)	T (K)	d^b	$\eta^c \times 10^{-2}$	d^b	$\eta^c \times 10^{-2}$
25	298	0.9005	3.0781	0.9125	5.2844
30	303	0.8865	2.4883	0.8996	3.8538
35	308	0.8738	1.8434	0.8862	3.0652
40	313	0.8612	1.4048	0.8705	2.2716
45	318	0.8463	1.1020	0.8572	1.7681
50	323	0.8335	0.8366	0.8423	1.3240

[a] t Is centigrade degree, Celsius, and T is absolute temperature, Kelvin degree.
[b] Density = d (g cm^{-3}).
[c] Viscosity = η (poise = g cm^{-1} s^{-1}).

where T is the absolute temperature (K), and k and l are the parameters of this equation (5). The values of the densities for unhydrogenated and hydrogenated sunflowerseed oils change linearly with temperature (Fig. 1). The slopes and intercepts of the plotted straight lines in Figure 1 give the values of l and k, respectively. The calculated values of k and l are 1.6977 and −2.6754 for unhydrogenated, and 1.7544 and −2.8223 for hydrogenated oil, respectively. Of the density parameters, k increases, but l decreases as the density increases, indicating a structural change during hydrogenation.

The energy of activation for viscous flow, $E^{\neq}$, presented by Glastone *et al.* (13), is given by:

$$E^{\neq} = R\frac{d\ \ln \eta}{d\ (1/T)} \quad [5]$$

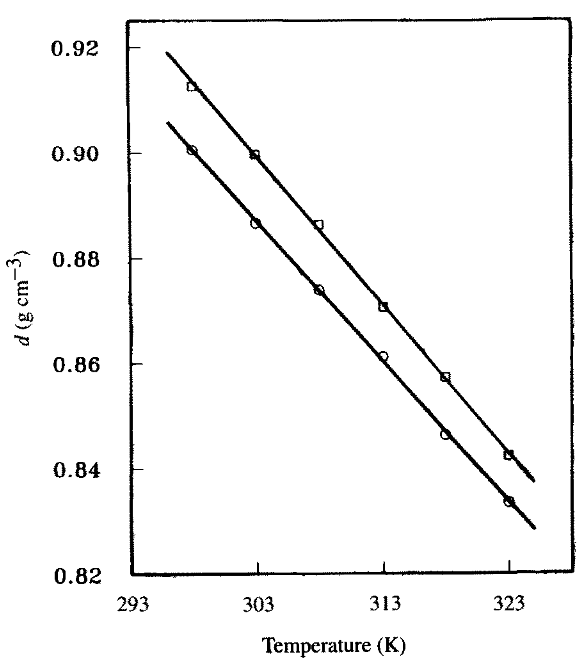

FIG. 1. Density (d) as a function of temperature: ○, unhydrogenated, and □, hydrogenated sunflower seed oil.

where R, η, and T are the gas constant, 8.314 J K^{-1} mol^{-1}, absolute viscosity, and absolute temperature, respectively. If ln η vs. $1/T$ is plotted according to Equation 5, $E^{\neq}/R$ represents the slope.

Figure 2 shows that the plot of ln η vs. $1/T$ is linear for unhydrogenated and hydrogenated sunflowerseed oils. The values of the activation energy for unhydrogenated and hydrogenated sunflowerseed oils have been calculated as 42.2 and 43.7 kJ, respectively. The activation energy of viscosity for unhydrogenated oil is less than for hydrogenated oil because unhydrogenated oil has more unsaturation with respect to hydrogenated oil. This can be seen from iodine values. The iodine value of unhydrogenated oil is higher than of hydrogenated oil (Table 1).

The free energy of activation for the viscous flow, $\Delta G^{\neq}$, proposed by Tanaka *et al.* (14), can be represented by the following equation:

$$\Delta G^{\neq} = R\ T\ \ln \frac{\eta V}{hN} \qquad [6]$$

where h is the Planck constant, 6.626×10^{-34} Js, N is the Avogadro number, 6.022×10^{23} mol^{-1}, and V is the molar volume of the moving unit (0.3098 $Lmol^{-1}$ and 0.3067 $Lmol^{-1}$ for unhydrogenated and hydrogenated sunflowerseed oils, respectively). The molar volume is the ratio of M/d, where M is molecular weight and d is density. For the calculation of the molar volume, for example, if the molecular weight and the density of unhydrogenated sunflowerseed oil are 278.9891 g mol^{-1}

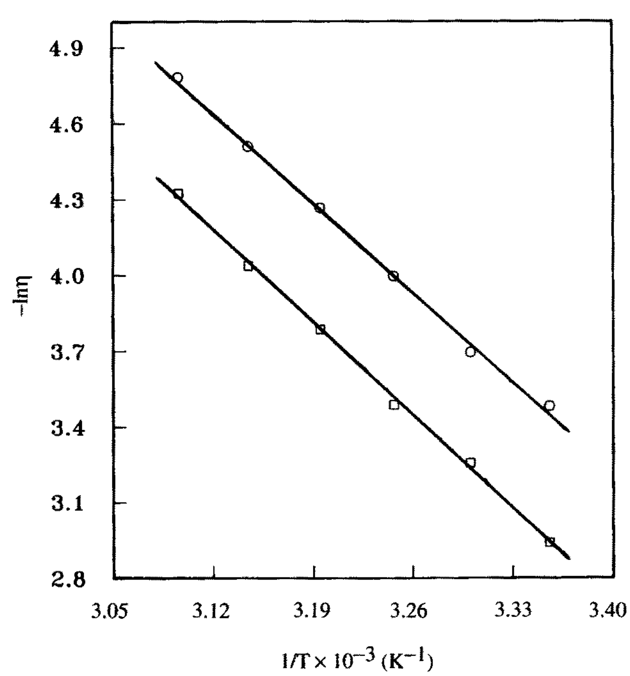

FIG. 2. The plot of ln η vs. $1/T$: ○, unhydrogenated, and □, hydrogenated sunflower seed oil.

and 0.9005 g mL^{-1}, respectively, at 25°C, the molar volume is calculated as 0.3098 $Lmol^{-1}$.

The activation free energies for unhydrogenated and hydrogenated sunflowerseed oils at 25°C have been found as 36.4 and 37.7 kJ mol^{-1}, respectively. It can be seen from these values that the activation free energy of oil increases as the unsaturation of oil decreases. According to the Eyring rate process approach to viscous flow (13), at equilibrium the potential barriers to movement are equal in all directions, but when a shearing force is imposed on a liquid, molecules moving in the direction of shear will be given an extra energy increment, so that net movement is produced. The shearing force mentioned is thought to be created due to hydrogenation.

The entropy of activation for viscous flow also may be calculated as:

$$\Delta S^{\neq} = \frac{E^{\neq} - \Delta G^{\neq}}{T} \qquad [7]$$

By means of Equation 7, the activation entropies of unhydrogenated and hydrogenated sunflowerseed oils at 25°C are 19.5 J and 20.1 J K^{-1}, respectively. The fact that the activation entropy increases after hydrogenation confirms that each double bond in each fatty acid may be isomerized or hydrogenated during hydrogenation.

The amount of structure in sunflowerseed oil will depend on both temperature and composition. Temperature will affect the structure through the amount of thermal movement. Composition alters structural characteristics by reason of hydrogenation. For both effects, the magnitude of the entropy change will be dependent on the amount of structure present.

Finally, we conclude that density and viscosity of an oil increase by hydrogenation. Because a more viscous oil is obtained from hydrogenation, its fluidity decreases. The viscosity of hydrogenated oil is approximately two times that of the unhydrogenated at each temperature (Table 2).

REFERENCES

1. Gouw, T.H., J.C. Vlugter and C.J.A. Roelands, *J. Am. Oil Chem. Soc. 43*:433 (1966).
2. Gouw, T.H., and J.C. Vlugter, *Ibid. 41*:142 (1964).
3. Gros, A.T., and R.O. Feuge, *Ibid. 29*:313 (1952).
4. Bonhourst, C.W., P.M. Althouse and H.O. Triebold, *Ind. Eng. Chem. 40*:2379 (1948).
5. Liew, K.Y., C.E. Seng and L.L. Oh, *J. Am. Oil Chem. Soc. 69*:155 (1992).
6. Kapseu, C., G.J. Kayem, D. Balesdent and L. Schhuffenecker, *Ibid. 68*:128 (1991).
7. *Bailey's Industrial Oil and Fat Products,* Vol. 2, edited by D. Swern, John Wiley and Sons, New York, 1982, pp. 1–14.
8. Kaimal, T.N.B., and G. Lakshminarayana, *J. Am. Oil Chem. Soc. 56*:578 (1979).
9. Morrison, W.H. III, and J.A. Robertson, *Ibid. 55*:20 (1978).

10. Daniels, F., J.W. Williams, P. Bender, R.A. Alberty, C.D. Cornwell and J.E. Harriman, *Experimental Physical Chemistry,* McGraw-Hill Book Co., New York, 1970, pp. 161–167.
11. Crockford, H.D., and J.W. Nowell, *Laboratory Manual of Physical Chemistry,* John Wiley and Sons, New York, 1965, pp. 55–58.
12. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* revised edition, Chicago, 1947, Methods Cd 1-25, Cc 1-25, Cd 14-61.
13. Glastone, S., K.J. Laidler and H. Eyring, *The Theory of Rate Processes,* McGraw-Hill Book Co., New York, 1941.
14. Tanaka, M., S. Kaneshina, W. Nishimoto and H. Takabatake, *Bull. Chem. Soc. Jpn 46*:364 (1973).

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