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DENSITIES AND REFRACTIVE INDICES OF HYDROGENATED PALM OLEIN AND FRACTIONATED PALM OIL

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The densities and the refractive indices of seven samples of neutralized, hydrogenated palm olein and six fractions from palm oil were determined. It was found that both the density and the refractive index decreased linearly with increasing temperature over the range 30°C to 80°C. The temperature coefficients for these properties were determined for both groups of samples. These properties were also found to be linearly dependent on the iodine values. Equations were developed for the two properties for each group of samples. These equations accurately predict the densities and the refractive indices for all the samples at the temperatures studied.

INTRODUCTION

The density and refractive index are easily determined characteristics of fats and oils and their derivatives. Accurate density determination is important because the trade in bulk oil is based upon weight whereas volume is actually being measured. Accurate refractive indices are useful for identification purposes and for establishing purity, as well as for following the progress of reactions such as catalytic hydrogenation and isomerization.

For liquid oils, it is generally known that, at constant temperature, the density increases with increase in unsaturation and decreases with increase in molecular weight. On the other hand, the refractive index increases with the length of the hydrocarbon chain as well as with the increase in the number of double bonds in the molecules (Formo, 1979). Thus approximate expressions have been developed

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for the specific gravity and refractive index of different oils at specific temperatures in terms of the saponification value and the iodine value (Gouw and Vlugter, 1964 and Pantzaris, 1985). The densities and refractive indices of some liquid oils and their derivatives at different temperatures have also been tabulated (Formo, 1979). It is also generally known that these properties vary linearly with temperature within a limited range of temperatures. We have recently developed simple equations, one for each of the series of n-alkanoic acids (Liew, *et al.* 1991), their methyl and ethyl esters (Liew and Seng, 1992), the n-alkylamines (Liew, *et al.* 1994) and the n-alkanols (Liew, *et al.* 1992) which predicted accurately the molal volumes of the members of these homologous series at different temperatures.

As with many other natural products, palm oil and its fractions do not have definite compositions and their properties vary within ranges of values. The iodine values of palm oil fractions vary from 48 to 58 for refined palm oil and palm olein from between 27 to 55 for palm stearin. The saponification values vary from 193 to 206 for both the palm olein and palm stearin (Tan and Oh, 1981). Moreover the densities and refractive indices vary from batch to batch. Although the values of these properties have been reported, no systematic study has been conducted. It was thus the purpose of this investigation to study the relationships between these properties and unsaturation and temperature, and to develop equations for the prediction of these properties.

EXPERIMENTAL

A sample of palm olein was used to produce hydrogenated products. It has an FFA content of 0.13%, a saponification value of 195.5 and an iodine value of 58.8; 400 ml of this olein was hydrogenated by means of a commercial nickel catalyst at 300°C and 20 psi of hydrogen. A 2-litre continously stirred reactor was used. Seven samples of about 40 ml each were collected at different reaction times. This samples were then treated by dissolving 15 ml portions in 50 ml hexane in the presence of 10 g of dried alumina. The alumina was then removed by filtration. The solvent was removed by rotary evaporation. The samples were then out-gassed and dried with an activated molecular sieve. The treated samples were found to have less than 0.04 % of FFA: much of the FFA originally present, as well as that formed during hydrogenation, had been adsorbed on the alumina.

The RBD palm oil used in this work had a saponification value of 203.4. Six fractions were obtained from the oil by fractionating aliquots of 100 ml at different temperatures. The different fractions of the oil were out-gassed and dried with molecular sieve before being used.

The density measurements were done by means of a pycnometer, while a white light source (tungsten lamp) was used to determine the refractive index. The temperature of the water bath used in this work was accurate to ± 0.05°C.

RESULTS AND DISCUSSION

The densities and refractive indices of the seven samples of hydrogenated palm olein described above were determined at 60°C, 65°C, 70°C, 75°C and 80°C. The saponification and iodine values of the samples were also determined. No significant changes in saponification values between the samples were observed.

The iodine values decreased with time of reaction, as expected. The densities and the refractive indices together with the iodine values are shown in *Tables 1* and *2*.

A sample of RBD palm oil with a saponification value of 203.4 was fractionated into six fractions. These contained a negligible amount of free fatty acid and their saponification values did not vary significantly from that of the original oil. The densities and refractive indices at temperatures between 30°C and 70°C were determined and are shown in *Tables 3* and *4* together with their iodine values.

Density

It is obvious from the data that the apparent densities of the neutralized hydrogenated palm

TABLE 1. DENSITIES OF NEUTRALIZED, HYDROGENATED PALM OLEIN SAMPLES

Sample	Iodine value	Saponification value		Temperature (°C)				
				60	65	70	75	80
1	46.65	196.22	a)	0.8818	0.8785	0.8750	0.8716	0.8682
			b)	0.8818	0.8784	0.8750	0.8715	0.8681
2	35.63	195.94	a)	0.8807	0.8774	0.8740	0.8707	0.8673
			b)	0.8807	0.8773	0.8739	0.8704	0.8670
3	26.98	195.77	a)	0.8799	0.8764	0.8731	0.8696	0.8661
			b)	0.8798	0.8764	0.8730	0.8696	0.8661
4	14.31	195.23	a)	0.8884	0.8750	0.8716	0.8681	0.8648
			b)	0.8785	0.8751	0.8717	0.8683	0.8649
5	6.20	195.41	a)	0.8776	0.8742	0.8708	0.8673	0.8639
			b)	0.8777	0.8743	0.8709	0.8675	0.8641
6	2.38	194.94	a)	–	0.8740	0.8709	0.8675	0.8641
			b)	–	0.8739	0.8705	0.8671	0.8635
7	2.20	195.78	a)	–	0.8741	0.8707	0.8672	0.8637
			b)	–	0.8739	0.8705	0.8671	0.8637

a) Experimental value
b) Calculated according to Equation 2

TABLE 2. REFRACTIVE INDICES OF NEUTRALIZED, HYDROGENATED PALM OLEIN SAMPLES

Sample	Iodine value		Temperature (°C)				
			60	65	70	75	80
1.	46.65	a)	1.4493	1.4474	1.4457	1.4439	1.4421
		b)	1.4496	1.4478	1.4459	1.4441	1.4423
2.	35.63	a)	1.4489	1.4470	1.4452	1.4434	1.4414
		b)	1.4487	1.4468	1.4450	1.4432	1.4414
3.	26.98	a)	1.4479	1.4460	1.4442	1.4423	1.4404
		b)	1.4479	1.4461	1.4443	1.4425	1.4406
4.	14.31	a)	1.4469	1.4450	1.4433	1.4415	1.4396
		b)	1.4469	1.4451	1.4432	1.4414	1.4396
5.	6.20	a)	–	1.4442	1.4424	1.4406	1.4389
		b)	–	1.4439	1.4420	1.4401	1.4383
6.	2.38	a)	–	1.4439	1.4420	1.4401	1.4383
		b)	–	1.4441	1.4422	1.4403	1.4386
7.	2.20	a)	–	1.4440	1.4421	1.4403	1.4383
		b)	–	1.4441	1.4422	1.4404	1.4386

a) Experimental value
b) Calculated according to Equation 4

TABLE 3. DENSITIES OF RBD PALM OIL FRACTIONS

Fraction	Iodine value		Temperature (°C)				
			30	40	50	60	70
1	62.8	a)	0.9049	0.8983	0.8917	0.8850	0.8782
		b)	0.9046	0.8980	0.8913	0.8847	0.8780
2	55.9	a)	0.9038	0.8974	0.8907	0.8840	0.8773
		b)	0.9039	0.8973	0.8906	0.8843	0.8773
3	55.3	a)	0.9035	0.8967	0.8901	0.8835	0.8768
		b)	0.9038	0.8971	0.8906	0.8839	0.8772
4	45.8	a)	–	–	0.8902	0.8836	0.8769
		b)	–	–	0.8897	0.8830	0.8764
5	41.7	a)	–	–	0.8895	0.8830	0.8762
		b)	–	–	0.8892	0.8825	0.8759
6	40.0	a)	–	–	0.8888	0.8822	0.8754
		b)	–	–	0.8890	0.8824	0.8757

a) Experimental value
b) Calculated according to Equation 3

TABLE 4. REFRACTIVE INDICES OF RBD PALM OIL FRACTIONS

Fraction		Temperature (°C)				
		30	40	50	60	70
1	a)	1.4619	1.4581	1.4546	1.4508	1.4473
	b)	1.4615	1.4579	1.4543	1.4507	1.4471
2	a)	1.4619	1.4581	1.4546	1.4508	1.4473
	b)	1.4614	1.4579	1.4543	1.4507	1.4471
3	a)	1.4519	1.4579	1.4546	1.4510	1.4474
	b)	1.4522	1.4584	1.4550	1.4515	1.4460
4	a)	–	–	1.4531	1.4495	1.4460
	b)	–	–	1.4530	1.4494	1.4458
5	a)	–	–	1.4527	1.4490	1.4455
	b)	–	–	1.4530	1.4490	1.4455
6	a)	–	–	1.4528	1.4493	1.4457
	b)	–	–	1.4528	1.4492	1.4456

a) Experimental value
b) Calculated according to Equation 5

olein and the fractions RBD palm oil decreased with increasing temperature and with decreasing iodine value. When the density was plotted as a function of temperature, straight lines were obtained for all the samples studied. We can thus write,

$$d = c - mT \quad (1)$$

where d is the density, c is a constant which depends upon the iodine value, m is the temperature coefficient and t is the temperature in °C. These values were determined using linear least square fitting and are shown in *Tables 5* and *6*. The temperature coefficients for the two series of oils distribute around their respective mean values randomly. The different mean values have no obvious relation to the iodine values. Using the respective mean temperature coefficients, the c values were plotted against the iodine values for the hydrogenated samples: a gradient of 1.0×10^{-4} per unit of iodine value and an intercept at 0.9181 g cm^{-3} were obtained by least square fit.

TABLE 5. VALUES OF C AND M IN EQUATION 1 FOR NEUTRALIZED HYDROGENATED PALM OLEIN SAMPLES

Samples	c (g cm^{-3})	10^4m(g cm^{-3} °C^{-1})
1	0.92276	6.82
2	0.92092	6.70
3	0.92118	6.88
4	0.91932	6.28
5	0.91878	6.86
6	0.91924	6.94
7	0.91820	6.80
Average		6.83

TABLE 6. VALUES OF C AND M IN EQUATION 1 FOR RBD PALM OIL FRACTIONS

Fraction	c (g cm^{-3})	10^{+4} m (g cm^{-3} °C^{-1})
1	0.92497	6.67
2	0.92384	6.64
3	0.92342	6.60
4	0.92347	6.70
5	0.92233	6.70
6	0.92280	6.65
Average		6.65

For the fractions from RBD palm oil, the variation in the iodine values was too small to enable the coefficient to be evaluated. For this series, the same gradient was used and the value of the average intercept calculated to be 0.9183 g cm^{-3}. Combining these values and equation 1, we obtained equations 2 and 3.

For the neutralized hydrogenated palm olein,

$$d = 0.9181 + 1.0 \times 10^{-4} \times IV - 6.83 \times 10^{-4} \times t \quad (2)$$

For the fractionated RBD palm oil

$$d = 0.9183 + 1.0 \times 10^{-4} \times IV - 6.65 \times 10^{-4} \times t \quad (3)$$

where d, IV and t are the density (g cm^{-3}), the iodine value and the temperature in °C respectively. When these equations were used to recalculate the densities of the hydrogenated oil, the maximum difference between the calculated and the experimental values was 0.0003, with the sample standard deviation of 0.0001. For the fractionated oil the sample standard deviation was 0.00016. These errors are within the accuracy of the experimental procedure. When the above equations are compared with an equation developed for triglyceride oils in general, (Pantzaris, 1985), it is seen that while the temperature coefficient for equation(2) is similar, the coefficient for IV of our equations is slightly lower and the constants are slightly higher than in the Pantzaris equation, possibly because we have developed the equations specifically for palm oils.

Refractive index

It is observed that the refractive indices of the samples decrease with increasing in temperature and with decreasing in iodine values, showing a similar trend to that of the densities. For the hydrogenated oils and the fractionated oils, plots of refractive index with temperature were straight lines with average gradients of 3.65×10^{-4}/°C and 3.59×10^{-4}/°C respectively, using least square fit. Using a procedure similar to that described for evaluating the density, two equations were developed to correlate the refractive index, r, with the iodine value and temperature. These are shown as equations (4) and (5).

For the neutralized hydrogenated oils:

$$r = 1.4676 + 8.34 \times 10^{-5} \times IV - 3.65 \times 10^{-4} \times t \quad (4)$$

For the fractionated oils:

$$r = 1.4669 + 9.65 \times 10^{-5} \times IV - 3.59 \times 10^{-4} \times t \quad (5)$$

When the calculated refractive indices were compared with the experimental values, good agreements were obtained in almost all cases, except for the first fraction from the RBD oil which had an iodine value of 62.8. The average error for this sample is 0.0005 unit which is slightly higher than can be accounted for in relation to the instrumental precision. Taking all the data into consideration, the sample standard deviations for the hydrogenated and fractionated oils are 0.0001 and 0.0005 respectively.

CONCLUSION

Two sets of equations which correlate the densities and the refractive indices of hydrogenated palm olein samples and fractions from palm oil with the iodine values and the temperature for the two groups of palm oil samples were developed.

These equations predict almost precisely the density and refractive index of the hydrogenated olein and the fractionated RBD palm oils in the temperature ranges studied. It can be seen that the temperature coefficients for both of the properties vary slightly between the series. These variations are likely to be the result of the slight differences in composition. During hydrogenation of palm olein, a small amount of free fatty acids (up to 0.8 %) was produced progressively. Although the free fatty acids were removed, the additional amount of diglycerides presumably formed could have caused the small variation in the temperature coefficients of both the density and the refractive index. However, if the average values of the two density equations are used, the calculated densities for the samples will show a deviation of approximately 0.0005. The densities so calculated will still be accurate within the third decimal place. A similar range of errors will also be obtained if a single average equation is used for the calculation of the refractive indices of the two samples. It must however be emphasized that the equations were derived for the temperature range studied. Outside this range, the density may no longer be in a strictly linear relationship with temperature. However, the equations can still be used to calculate an approximate density value and refractive index for a palm oil sample with a known iodine value.

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