Acta Chim. Slov. **1999**, *46*(4), pp. 511-521

CHARACTERISTICS OF VEGETABLE OILS OF SOME SLOVENE MANUFACTURERS†

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(Received 6.7.1999)

ABSTRACT

Eleven samples of vegetable oils were examined and the following indices determined: peroxide value, acid value, iodine value, saponification number, specific gravity, refractive index at 298.15 K and electric permittivity in the temperature range from 298.15 to 313.15 K. Some empirical relations between physical and chemical constants were fitted to the experimental data and the correlation constants for the best fit are presented. In addition, the correlation constants for calculating the electric permittivity of oils in the range of temperature from 298.15 to 313.15 K were obtained and the effective dipole moment was estimated via *Debye*'s equation.

INTRODUCTION

Edible oils extracted from plant sources are important in foods and in various other industries (e. g. cosmetics, pharmaceuticals, lubricants). They are key components of the diet and also provide characteristic flavours and textures to foods. During extraction, purification and usage, oils undergo a variety of processing operations, including heating, distillation and chemical modification which may alter their properties.

† Dedicated to Professor Drago Leskovšek on his 80th birthday

Several semi-empirical equations have been developed that relate the property of interest (e. g. time for fat to drain from a fried potato chip) to independently measurable bulk properties (e.g., density, viscosity, surface tension, etc). With these equations, it is possible to predict how changes in the properties of an oil alter the efficacy of a process without resorting to time-consuming trial-and-error experiments. The chemical and physical properties of edible oils depend primarly on composition (and hence on biological origin) and temperature. In this work, we have compiled some bulk parameters for different vegetable oils of some Slovene manufacturers with special focus on dielectric properties of oils because of the lack of corresponding data.

EXPERIMENTAL

Samples for examination were obtained from a commercial centre and represent three Slovene manufacturers, i. e. GEA Oil Factory, Slovenska Bistrica (G), Oil Factory Domžale (D) and Mercator-Oljarica Kranj (K). The fatty acid composition and source or manufacturer of each vegetable oil are shown in Table 1.

Chemical constants of oils

The following chemical determinations were carried out according to the methods described in the A. O. A. C. [1]: peroxide value, acid value, iodine number, and saponification number. All tests were performed in triplicate.

Physical characteristics of oils

Density measurements were carried out using a pycnometer at a temperature of 298.15± 0.05 K; the pycnometer of capacity about 25 cm^3 being calibrated with water [2]. The relative error in the density, $\frac{\delta\rho}{\rho}$, was estimated by the expression

$$\frac{\delta\rho}{\rho} = \frac{\delta m}{m} + \frac{\delta m_o}{m_o} + \frac{\delta m_p}{m_p} \quad (1)$$

where m, m_o and m_p are the mass of the pycnometer when filled with oil, water and air, respectively and $\delta m = \delta m_o = \delta m_p = 0.0001$ g are their uncertainities. The relative error in the density of water, $\frac{\delta\rho_o}{\rho_o}$, was considered to be a negligible quantity in comparison with the others.

Table 1. Fatty acid distributions and sources of vegetable oils.

Sample	Specification and source or manufacturer	Composition (%)[a]		
		Saturated	Monounsaturated	Polyunsaturated
1	Refined sunflower oil (99%) and wheat germ oil (1%); G	< 20	NA[c]	NA[c]
2	Nonrefined sunflower oil (cold pressed); G	10	25	65
3	Refined corn germ oil (99%) and wheat germ oil (1%); G	< 20	NA[c]	NA[c]
4	Refined extra sunflower oil (high level of oleic acid); G	10[b]	80[b]	10[b]
5	olive oil (natural + refined); G	20 (palmitic acid)	55-83 (oleic acid)	3.5-21 (linoleic acid)
6	Refined sunflower oil (100%); G	10[b]	20[b]	70[b]
7	mixed salad oil; D	10-12	17-25	>60
8	Unrefined olive oil (cold pressed); D	8-27	55-83	4-20
9	Refined sunflower oil; D	NA[c]	NA[c]	>55 (linoleic acid)
10	Refined sunflower oil (100%); K	9-17	17-40	48-70
11	Refined corn germ oil; K	10-15	20-35	50-60

[a] Provided by the manufacturers. [b] Approximate values. [c] Not available.

The refractive index of the samples was measured at 298.15 ± 0.05 K with a *Carl Zeiss Abbé* refractometer (32-G 110e) with a precision of $1 \cdot 10^{-4}$ at a wavelength of 589 nm.

Electric permittivity (*dielectric constant*) *measurements* were carried out at temperatures from 298.15 ± 0.05 K to 313.15 K in 5 K intervals using a WTW dipolemeter (model DM 01) with a DFL 1 cell at a constant frequency of 2 MHz. The calibration of the cell (25 cm^3) was performed as in reference [3], with benzene, carbon tetrachloride and cyclohexane as standards. The standard error of the estimate of electric permitivitty, ε, was about $1.3 \cdot 10^{-3}$.

RESULTS AND DISCUSSION

The results of chemical analysis in Table 2 indicate that the characteristics of eleven selected edible oil samples are in agreement with current published values for these indices. Values are typical rather than average and variations may occur , depending on a number of variables such as source, treatment, and age of the oil. Thus, the iodine values, *IV* (g_{I_2} / 100 g_{sample}) for olive oils (samples 8 and 4) are noticeably lower than for the other kinds of oil but within the limits of the literature data (77-95, [4]). The saponification values, *SV* (mg $_{KOH}$ /g $_{sample}$), varying slightly from 191.4 for corn germ oil (sample 3) to 193.9 for olive oil (sample 5), show that the fatty acids present in these oils have a high number of carbon atoms. Quality evaluation through acid value, *AV* (mg $_{KOH}$ /g $_{sample}$) and the peroxide value, *PV* (mmol $_{peroxide}$ / kg $_{sample}$) confirmed that the quality of these oils was satisfactory. Freshly deodorized oil should have zero *PV*, but in most cases, for the product to have acceptable storage stability the *PV* of oils used should be less than 5. Olive oil contains components that interfere with conventional *PV* determination; even freshly pressed olive oils have *PV* values of about 5, and under certain climatic conditions (dry weather) the *PV* value can be higher than 5 [5].

The density data are presented in Table 3. On average, the relative error of the density, calculated via relation (1), amounts to $1.0 \cdot 10^{-5}$ meaning that the density values were accurate to five decimal places. The relative density or specific gravity of an oil at any given temperature compared to water at a specified temperature is known to increase as the mean molecular weight diminishes (i. e. with higher *SV*), and also as the degree of unsaturation increases (i. e. with higher *IV*) [4]. For the samples investigated the following expression for the approximate specific gravity, d_{25}^{25} was developed

$$d_{25}^{25} = 0.83088 + 0.000306 \cdot SV + 0.000271 \cdot IV \qquad (2)$$

on the basis of multiple linear regression analysis; the standard error of the estimate *s* was found to be $1.4 \cdot 10^{-4}$ and the determination coefficient greater than 0.999.

Table 2. Chemical characteristics of the edible oils studied.

Sample	Characteristics			
	Peroxide value ($mmol_{peroxide}$ / kg_{sample})	Iodine value (g_{I_2} / 100 g_{sample})	Acid value (mg_{KOH} / g_{sample})	Saponification value (mg_{KOH} /g_{sample})
1	2.026±0.002	112.444±0.018	0.2120±0.0001	191.65±0.04
2	1.788±0.002	111.043±0.009	1.3442±0.0004	192.07±0.02
3	1.780±0.001	108.593±0.003	0.1294±0.0001	191.44±0.02
4	2.178±0.001	87.738±0.006	0.2785±0.0003	191.46±0.02
5	3.287±0.002	84.638±0.006	0.8293±0.0003	193.95±0.04
6	1.962±0.001	109.860±0.006	0.1954±0.0003	192.55±0.05
7	1.980±0.001	108.658±0.007	0.2286±0.0002	191.72±0.05
8	7.493±0.002	82.553±0.008	2.5987±0.0010	191.62±0.02
9	2.227±0.001	109.380±0.008	0.1784±0.0001	192.26±0.03
10	2.146±0.001	109.231±0.007	0.1144±0.0001	191.85±0.04
11	1.707±0. 001	110.116±0.002	0.1137±0.0001	191.87±0.02

Table 3. Density, relative density, refractive index and specific refraction of edible oil samples at 298.15 K.

Sample	ρ / g cm^{-3}	d_{25}^{25}	n_D	r / cm^3 g^{-1}
1	0.91710	0.91981	1.4736	0.30622
2	0.91688	0.91960	1.4734	0.30618
3	0.91655	0.91926	1.4727	0.30557
4	0.91047	0.91316	1.4681	0.30537
5	0.91037	0.91307	1.4674	0.30502
6	0.91685	0.91956	1.4731	0.30603
7	0.91674	0.91946	1.4728	0.30590
8	0.90934	0.91203	1.4669	0.30508
9	0.91683	0.91955	1.4731	0.30601
10	0.91678	0.91949	1.4729	0.30594
11	0.91680	0.91951	1.4730	0.30599

The refractive indices of the oils investigated, n_D, at 298.15 K are given in Table 3, and tend to increase with the number of double bonds, i. e. with mean unsaturation or iodine value, *IV*. In general, the refractive indices of natural fats and oils are related to their average degree of unsaturation in an approximately linear way. The relationship between refractive index and the iodine, acid, and saponification values is somewhat more complex. A number of equations have been proposed which are of limited application and fair accuracy, e. g. [4]. The relationship between refractive index and iodine value of the oils investigated has the form

$$n_D^{25} = 1.4484 + 0.0002247 \cdot IV \qquad (3)$$

and a more general relationship was found to be

$$n_D^{25} = 1.4446 + 0.000019 \cdot SV + 0.0042 \cdot \frac{AV}{SV} + 0.000226 \cdot IV \qquad (4)$$

The standard error of the estimate, s was found to be $6.6 \cdot 10^{-5}$ and $7.2 \cdot 10^{-5}$ for rels. (3) and (4) respectively, while the determination coefficient was 0.9997 in both cases.

Related to the refractive index is the specific refractivity; the dependence of the refractive index upon specific volume has been related by the equation $r = (n_D - 1)/\rho$, where *r* is the specific refraction. A more useful relation is the *Lorenz-Lorentz* equation [6]

$$r = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{\rho} \tag{5}$$

which was used for calculating the values of r for the oil samples in Table 3. It seems that specific refraction is not a particulary distinguishing characteristic of the investigated edible oils; namely, $\bar{r}$ = 0.30579 ± 0.00043 $cm^3\ g^{-1}$.

The dielectric data obtained for eleven edible oils are recorded in Table 4; the values of electric permittivity, ε, lie in the range of about 3.0-3.2 (at 298.15 K) as is usually the case for most oils. It is evident that electric permittivity increases somewhat with increase in the unsaturation of the oil, i. e. with *IV* (see Table 2) and decreases with increasing temperature. The variation of electric permittivity with temperature for the oils investigated is given by

$$\varepsilon = \varepsilon_o + a_1(T - T_o) + a_2(T - T_o)^2 \tag{6}$$

where *T* is the absolute temperature, T_o is 298.15 K while ε_o, a_1 and a_2 are empirical constants which were obtained by the method of least squares [7] on the basis of the data in Table 4. The relevant standard error of the estimate, *s* is given in Table 5. From Table 5 it is evident that the values of the constant ε_o, within experimental error, are equal to the electric permittivity of an oil at 298.15 K, while the values of a_1 are negative; in contrast, all the a_2 values are positive.

The coefficient of temperature dependence of electric permittivity, γ, was calculated via the relation

$$\gamma = -\frac{1}{\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_P \tag{7}$$

From equation (7) it is apparent that the relative change in electric permittivity, $\frac{\partial \varepsilon}{\varepsilon}$, is proportional to the variation of temperature, and the coefficient of proportionality is

Table 4. Change in electric permittivity of edible oils with temperature.

Sample	ε			
	298.15 K	303.15 K	308.15 K	313.15 K
1	3.161	3.110	3.080	3.071
2	3.160	3.123	3.091	3.061
3	3.150	3.106	3.075	3.059
4	3.105	3.067	3.038	3.016
5	3.098	3.067	3.036	3.007
6	3.159	3.121	3.092	3.075
7	3.153	3.116	3.087	3.067
8	3.093	3.070	3.048	3.026
9	3.158	3.115	3.085	3.068
10	3.157	3.116	3.085	3.066
11	3.156	3.116	3.085	3.062

Table 5. Values of regression coefficients of equation (6) for the oil samples studied, together with the standard error of the estimate, *s*.

Sample	ε_o	$-a_1 \cdot 10^3$	$a_2 \cdot 10^4$	$s \cdot 10^4$
1	3.1610 ± 0.0000	12.3 ± 0.00	4.20 ± 0.00	± 0.00
2	3.1598 ± 0.0007	7.63 ± 0.21	7.00 ± 0.13	± 6.71
3	3.1501 ± 0.0004	10.28 ± 0.14	2.80 ± 0.09	± 4.47
4	3.1049 ± 0.0004	8.32 ± 0.14	1.60 ± 0.09	± 4.47
5	3.0981 ± 0.0004	6.38 ± 0.14	0.20 ± 0.09	± 4.47
6	3.1591 ± 0.0003	8.83 ± 0.10	2.15 ±0.07	± 3.35
7	3.1531 ± 0.0002	8.29 ± 0.07	1.70 ± 0.04	± 2.24
8	3.0929 ± 0.0002	4.61 ± 0.07	0.10 ± 0.04	± 2.24
9	3.1580 ± 0.0000	9.90 ± 0.00	2.60 ± 0.00	± 0.00
10	3.1571 ± 0.0004	9.38 ± 0.14	2.20 ± 0.09	4.47
11	3.1559 ± 0.0002	8.81 ± 0.01	1.70 ± 0.04	± 2.24

equal to the coefficient of temperature dependence of electric permittivity. Through relations (6) and (7) the coefficient γ of an oil is given by

$$\gamma = -\frac{1}{\varepsilon}\left[a_1 + 2a_2\left(T - T_o\right)\right] \tag{8}$$

At the temperature of 298.15 K equation (8) simplifies to

$$\gamma_o = -\frac{a_1}{\varepsilon_o} \tag{9}$$

The error in the coefficient, $\delta\gamma_o$ was obtained as

$$\delta\gamma_o = \frac{\delta a_1 \gamma_o + a_1 \delta\gamma_o}{\varepsilon_o^2} \tag{10}$$

where δa_1 and $\delta\varepsilon_o$ are the errors in the relevant parameters. The values of the thermal coefficient γ_o for the oil samples are given in Table 6 and, ranging from $1.49 \cdot 10^{-3}$ K^{-1} (sample 8) to $3.89 \cdot 10^{-3}$ K^{-1} (sample 1), seem to follow the variations in unsaturation of the oils.

Table 6. Values of the coefficient of the temperature dependence of the electric permittivity, specific polarization, specific orientation polarization and effective dipole moment for the oils investigated at 298.15 K.

Sample	$(\gamma_o \pm \delta\gamma_o)\cdot 10^3$ / K^{-1}	p / cm^3 g^{-1}	p_o / cm^3 g^{-1}	μ / D
1	3.89 ± 0.00	0.4566	0.1503	2.54
2	2.41 ± 0.07	0.4565	0.1504	2.53
3	3.26 ± 0.04	0.4555	0.1499	2.54
4	2.68 ± 0.05	0.4529	0.1475	2.52
5	2.06 ± 0.05	0.4520	0.1470	2.50
6	2.80 ± 0.03	0.4564	0.1504	2.54
7	2.63 ± 0.02	0.4558	0.1499	2.54
8	1.49 ± 0.02	0.4519	0.1468	2.51
9	3.13 ± 0.00	0.4563	0.1503	2.54
10	2.97 ± 0.04	0.4562	0.1503	2.54
11	2.79 ± 0.02	0.4561	0.1501	2.54

From the values of electric permittivity of the oils investigated at 298.15 K the specific polarizations were calculated using the *Debye* equation

$$p = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{\rho} \tag{11}$$

Assuming that the difference between the specific polarization and refraction is a measure of the orientation polarization, i. e. $p_o = p - r$, then the effective dipole moment, μ, may be calculated from the orientation polarization as follows [8]

$$\mu^2 = \frac{9kT\overline{M}}{4\pi N} \cdot p_o \tag{12}$$

where *k* is the *Boltzmann* constant, *T* the absolute temperature, $\overline{M}$ the mean molecular weight and *N* the *Avogadro* number. Thus, in the case of edible vegetable oils, the effective dipole moment calculated in this manner represents the effective dipole moment of the large oil molecules or aggregates of molecules, regarded as rigid structures and rotating as such. The corresponding specific polarizations, specific orientation polarizations and effective dipole moments are listed in Table 6; the mean molecular weights of the samples studied, calculated via the relationship $\overline{M} \cdot SV = 168300$ [9], are rather close to each other, e. g. from 867.8 (sample 5) to 879.1 (sample 3). So it is evident that the effective dipole moment cannot be a satisfactory index either for identifying e. g. an olive oil, or for differentiating between sunflower and corn germ oils. Likewise the dielectric constant requires at least density and refractive index determinations for purposes of identification.

However, food oils in general exhibit significant variations in their composition; consequently, it is impossible to define unique values for chemical and physical constants for any oil and it is usually necessary to combine several empirical constants to predict the chemical and physical properties of edible oils. None of the data reported here represent a survey of the range of parameters for all varieties of a particular oil; so the degree of interspecies variability remains undefined.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Technology of the Republic of Slovenia.

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POVZETEK

Enajstim vzorcem jedilnega olja smo določili peroksidno število, kislinsko število, jodovo število, saponifikacijsko število, specifično težo, lomni količnik pri 298.15 K ter električno permitivnost v temperaturnem območju od 298.15 do 313.15 K. Preizkusili smo nekaj empiričnih relacij med fizikalnimi in kemijskimi konstantami, d oločili korelacijske konstante za izračun električne permitivnosti olj v temperaturnem intervalu od 298.15K do 313.15 K ter izračunali povprečni dipolni moment olj preko *Debye*ve relacije.