Rheological Studies and Characterization of Different Oils

[1]NAVEED AKHTAR*, [1]QAZI ADNAN, [1]MEHMOOD AHMAD,
[2]AHMAD MEHMOOD AND [3]KALSOOM FARZANA
[1]*Faculty of Pharmacy & Alternative Medicines, the Islamia University of Bahawalpur, Bahawalpur, Pakistan.*
[2]*College of Pharmacy, University of the Punjab, Lahore, Pakistan.*
[3]*Faculty of Pharmacy, Bahauddin Zakariya University, Multan, Pakistan.*

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Summary: As most of the natural oils are used in cosmetics, especially in emulsions, these oils produce direct effects on the consistency and shelf life of the emulsions. In case of w/o emulsion, higher the viscosity of the oil, higher is the viscosity of emulsion. Other parameters of oil like spreadability, cloud point, pour point, saponification value, acid value, pH and specific gravity of oils also affect properties of emulsions. The purpose of this study was the characterization of different oils and their rheological properties. Eight different natural oils, namely olive, coconut, almond, castor, sesame, cotton seed, sunflower, and paraffin oils were used to study their rheology, viscosity, spreadability, cloud and pour points, saponification and acid values, pH and specific gravity. All the oils investigated were found to possess Newtonian behaviour with little deviation in olive and coconut oils. Castor oil possesses the maximum viscosity of 686.26 mPas.s among the other oils studied. Paraffin oil containing no fatty acids possesses the maximum spreadability. Castor oil has the maximum saponification value (187.02), while the paraffin oil has minimum value of 32.70. Olive oil has the maximum acid value of 1.361 among the oils investigated while paraffin oil has the minimum value of 0.224. The pH of castor oil is maximum (4.92), while that of cotton seed oil is minimum being 3.64. Paraffin oil has the maximum specific gravity value of 0.9999 while coconut oil has the minimum value of 0.9138.

Introduction

The role of rheology is important in the field of cosmetic science, especially in the field of emulsions and lotions [1]. Since the different creams have different consistencies and they are used for long terms, the effects of different rheological parameters of oils are studied for the understanding the performance of the system [2].

There are two principal models of rheology, which are Newtonian and Non-Newtonian systems. Newtonian materials and products are whose viscosity remains constant by varying shear stresses. This type of flow is influenced by the variation in temperature. Viscosity, shear stress, shear rate, yield value, plastic, pseudoplastic and thixotropic models, viscometer and rheometer types are the major issues discussed in rheology [3].

The role of oils in cosmetics science and emulsion formulation is important. Oils have a great influence on the rheological behavior of emulsions. Usually, if the viscosity of oil is high, then the viscosity of the emulsion will also be high. Olive, coconut, almond, castor, sesame, cotton seed, sunflower, and paraffin oils are among the frequently used oils in emulsion formulation and therefore, selected for characterization. Different parameters like spreadability, cloud point, pour point, saponification value, acid value, pH, specific gravity and viscosity of the oils were determined. Natural oils have some added benefits for their use in cosmetic formulations, *e.g*, they are non-toxic, non-irritant, nourishing for skin, compatible with skin and beneficial for physiological functions of skin [4].

Results and Discussion

Characterization of Oils

Rheological properties of different oils, the effect of change in shear stress on shear rate were measured at 25 °C (Table-1).

Rheological Analysis

Flow Type

Newtonian or Non-Newtonian behavior is the most important physical property of the oils.

*To whom all correspondence should be addressed.

Table-1: Rheological parameters of different oils.

Sr. #	Olive Oil			Coconut Oil			Almond Oil			Castor Oil		
	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate (1/s)	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate(1/s)	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate (1/s)	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate (1/s)
1.	65.41	45.79	70.00	47.19	33.03	70.00	66.10	29.74	45.00	712.28	7.12	7.12
2.	63.24	47.43	75.00	45.08	33.81	75.00	66.06	33.03	50.00	700.53	14.01	14.01
3.	61.83	49.47	80.00	44.52	35.61	80.00	65.75	36.16	55.00	675.75	20.27	20.27
4.	61.14	51.97	85.00	44.29	37.65	85.00	65.75	39.45	60.00	684.88	27.40	27.40
5.	60.62	54.56	90.00	44.09	39.68	90.00	65.75	42.74	65.00	684.10	34.20	34.20
6.	60.31	57.30	95.00	44.08	41.88	95.00	65.52	45.87	70.00	682.27	40.94	40.94
7.	60.03	60.03	100.00	43.99	43.99	100.00	65.54	49.15	75.00	682.08	47.75	47.75
8.	60.01	63.01	105.00	44.06	46.26	105.00	65.45	52.36	80.00	680.97	54.48	54.48
9.	59.91	65.91	110.00	44.05	48.45	110.00	65.47	55.65	85.00	680.10	61.21	61.21
10.	59.90	68.88	115.00	44.10	50.72	115.00	65.40	58.86	90.00	679.40	67.94	67.94

Sr. #	Sesame Oil			Cottonseed Oil			Sunflower Oil			Paraffin Oil		
	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate(1/s)	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate(1/s)	Viscosity (mPas.s)	Shear Stress (D/cm²)	Shear Rate(1/s)	Viscosity (mPs.s)	Shear Stress (D/cm²)	Shear Rate (1/s)
1.	54.66	32.80	60.00	58.57	35.14	60.00	58.31	34.99	60.00	7.10	17.38	244.60
2.	54.43	35.38	65.00	58.40	37.96	65.00	58.28	37.88	65.00	7.12	17.85	250.72
3.	54.34	38.04	70.00	58.37	40.86	70.00	58.26	40.78	70.00	7.10	18.24	256.83
4.	54.37	40.78	75.00	58.23	43.68	75.00	58.23	43.68	75.00	7.08	18.63	262.94
5.	54.40	43.52	80.00	58.31	46.65	80.00	58.21	46.57	80.00	7.10	19.10	269.06
6.	54.33	46.18	85.00	58.20	49.47	85.00	58.20	49.47	85.00	7.08	19.49	275.18
7.	54.36	48.92	90.00	58.18	52.36	90.00	58.18	52.36	90.00	7.12	20.04	281.29
8.	54.30	51.58	95.00	58.09	55.18	95.00	58.17	55.26	95.00	7.11	20.43	287.41
9.	54.24	54.24	100.00	58.08	58.08	100.00	58.08	58.05	100.00	7.12	20.90	293.52
10.	54.27	56.98	105.00	58.00	60.90	105.00	58.07	60.97	105.00	7.13	21.37	299.64

When Newtonian liquids are subjected to shear stress, their viscosity does not change, however, the shear rate is changed or in other words, the shear stress and shear rate are directly proportional to each other in Newtonian liquids [5]. The profile of shear stress *versus* shear rate of Newtonian liquids gives a straight line. Newtonian liquids show an ideal flow, where shear stress is directly proportional to the shear rate;

$$\sigma = \eta\gamma$$

σ is the shear stress, γ is the shear rate and η is the absolute viscosity [6].

In this study, Newtonian or Non-Newtonian behaviors of different oils (olive, almond, coconut, castor, sesame, cotton seed, sunflower and paraffin) were investigation. Most of the oils used in this study show Newtonian behaviour. Behaviour of oils can be evaluated by applying the Power Law equation and calculation of their flow index (n). According to Power Law model, if the flow index (n) of a liquid is 1, then it is purely Newtonian and if the value of flow index deviates from 1 then it shows the Non-Newtonian behaviour. Table-2 shows that two oils (olive and coconut) have the flow index value deviating from 1 *i.e*, 0.84 and 0.90, respectively, approaching the Non-Newtonian behaviour. However, other oils have flow indices very close to 1 and hence they are Newtonian in nature. The confidence of fit values to Power Law model was found to be 98.9-100 for all the oils, showing maximum fit.

Table-2: Power Law Analysis of different oils at 25±0.1 °C.

Sr. #	Name of Oils	Consistency Index	Flow Index	Confidence of fit (%)
1	Olive Oil	124.7	0.84	99.0
2	Coconut Oil	96.4	0.90	98.9
3	Almond Oil	70.1	0.98	99.9
4	Castor Oil	705.6	0.98	99.4
5	Sesame Oil	56.7	0.99	99.9
6	Cottonseed Oil	62.3	0.98	99.9
7	Sunflower Oil	60.0	0.99	100.0
8	Paraffin Oil	6.55	1.01	99.8

Viscosity

It is known that the chain length, saturation, unsaturation and position of hydroxyl group of the fatty acids directly influence the viscosity of oils, hence the oils having greater chain length have greater viscosity [7] (Table-3).

Table-3: Classification of fatty acids according to chain length.

Group	Chain Length	Carbon Atoms
I	Short Chain Length	4-8
II	Medium Chain Length	8-12
III	Long Chain Length	12-22

As presented in Table-4, olive, almond, sesame, cotton seed and sunflower oils are in same range of viscosity (58-66 mPas.s). These oils mainly consist of long chain of carbon atoms (C-16 to C-18), but the coconut oil consists of short chain fatty acids and hence its viscosity is lower. Castor and paraffin oils also consist of long chain carbon atoms and therefore the viscosity of castor oil is high (686.236 mPas.s) which is highest value among the values of all the oils. However, paraffin oil has the lowest viscosity (7.11 mPas.s), among all other oils. The reasons for the highest value of viscosity of castor oil is: castor oil mainly consists of recinoleic acid, a mono-unsaturated 18-carbon fatty acid which has a hydroxyl group at the twelfth carbon, a very uncommon property for a biological fatty acids. This functional group causes recinoleic acid (thus castor oil) to be unusually polar, hence its properties deviate from other oils. On the other hand, paraffin oil having the lowest viscosity, also consists of 14-18 carbon atoms, however, it consists of only carbon and hydrogen atoms and does not contain the carboxyl and hydroxyl groups of fatty acids found in other vegetable oils.

Spreadability

The spreadability of an oil is in correlation with the subjective evaluation of penetration

Table-4: Average values of different parameters of different Oils.

Sr. #	Name of Oils	Average Viscosity (mPs.s)	Average Diameter (mm)	Cloud Point (°C)	Pour Point (°C)	Average Saponification Value	Average Acid Value	Average pH value	Average Specific gravity
1	Olive Oil	63.61	7.4	-11.1	-14.2	130.32	1.361	4.6206	0.9185
2	Coconut Oil	44.16	7.67	13.1	12.7	78.00	0.378	3.91	0.9138
3	Almond Oil	65.68	8.67	-13.8	-18.3	186.50	1.87	4.85	0.9209
4	Castor Oil	686.24	5.03	-18.2	-21.7	187.02	1.351	4.92	0.9598
5	Sesame Oil	54.37	8.33	-8.7	-11.8	117.48	0.547	3.80	0.9185
6	Cottonseed Oil	58.24	8.00	-0.5	-4.9	62.52	0.295	3.64	0.9186
7	Sunflower Oil	58.19	7.17	-9.5	-12.1	186.31	0.263	4.35	0.9175
8	Paraffin Oil	7.11	17.5	7.5	3.5	32.70	0.224	4.31	0.9999

capability in *Stratum corneum* and the time course of the greasy feeling. Since spreadability depends on external conditions such as temperature and atmospheric humidity, *in vitro* spreadability values were determined in a conditioned room of 40.7 % relative humidity and 25 °C temperature. The spreadability of the tested oil was assigned to a group according to the diameter found (Table-5) [8].

Table-5: Spreadability classification.

Group	Diameter	Spreadability
I	<10 mm	Low spreadability
II	10-13 mm	Moderate spreadability
III	13-16 mm	Good spreadability
IV	16-19 mm	Very good spreadability
V	>19 mm	Super spreadability

According to Table-4 the diameter of the spreading area of castor oil was found to be 5.03 mm which is the minimum spreadability among all the oils, while the remaining oils, olive, almond, coconut, sesame, cotton seed and sunflower also have the spreading diameters less than 10 mm showing low spreadabillity. Only the paraffin oil has 17.5 mm spreading diameter, showing very good spreadability. The spreadability of oils can be correlated with viscosity, greater the viscosity of oil, lower the spreadability and vice versa. Hence, the spreadability of oils indirectly has a correlation with the chain length of carbon atoms. The oils with long chain fatty acids will have low spreadability and the oils having shorter chain length will spread more.

Cloud Point and Pour Point

Cloud point of oil is defined as the temperature at which the substance becomes turbid on cooling (EN 23015). Pour point specifies the temperature at which the oil solidifies and is defined as the temperature on cooling, with 3 °C added thereto, at which the substance is no longer able to flow (DIN ISO 3016) [9]. Direct relationship between freeze stability of water-in-oil emulsions and pour point of the oils were reported [6]. Therefore, it was concluded that if the pour point of the oil is low, solidific ion point of the emulsion will be low and thus the freeze stability of the emulsion will be better.

According to Table-4 castor oil has the lowest cloud and pour points (-18.2 °C and -21.7 °C), respectively, while coconut oil has highest cloud and pour points (13.1 °C and 12.7 °C) among all the oils studied. The chain length of fatty acids affect the cloud and pour points of the oils. Olive, almond, sesame and sunflower oils contain long chain (18-carbon atoms) fatty acids and their cloud and pour points are between -9.5 °C - 18.3 °C. Cotton seed oil contains 16-18 carbon atom, therefore, its cloud and pour point is high (-0.5 °C and -4.9 °C). Coconut oil contains short chain (6-8) carbon atom fatty acids and therefore its cloud and pour points are the highest (13.1 °C and 12.7 °C) among all other oils. The cloud and pour points of paraffin oil (7.51 °C and 3.5 °C) are high due to no presence of fatty acids. Therefore, it can be concluded that shorter the chain length, higher the cloud point and pour points, and vice versa.

Viscosity also influences the pour and cloud points of the oils. As the viscosity of castor oil is higher (686.24 mPas.s) than the viscosity of any other oil, cloud and pour points (-18.02 °C and -21.7 °C) of this oil are the lowest among all the oils used in this study. The viscosity of paraffin oil is 7.11 mPas.s, which is the lowest viscosity among the viscosities of all other oils. However, its cloud and pour points are 7.5 °C and 3.5 °C, which are lower than that of coconut oil (13.1 °C and 12.7 °C). Although the viscosity of coconut oil (44.16 mPas.s) is higher than the viscosity of paraffin oil (7.11 mPas.s), its cloud and pour points (13.1 °C and 12.7 °C) are higher than the cloud and pour points of paraffin oil. The cloud and pour points of coconut oil may be higher due to the presence of saturated fatty acids (caproylic and caproyc acids), while saturated fatty acid is present in paraffin oil.

Saponification Value

The hydrolysis of fats with alkali resulting in the formation of salts of fatty acids (also called as soaps) and glycerol is called saponification. The amount in mg of KOH required to saponify 1 g of a fat is called the saponification value. Three molecules of KOH are consumed for saponification of each molecule of triacylglycerol, irrespective of the chain length of a fatty acid. Evidently, each gram of oil containing more amount of triacylglycerol will require much more KOH and hence its saponification value will be higher. The saponification value is thus an indication of average molecular weight of the fatty acid in an acylglyceride [10].

Table-4 demonstrates that paraffin and cotton seed oils have minimum saponification values of 32.70 and 62.52, respectively, showing that these oils contain minimum number of triacylglycerols. However, castor oil has the maximum saponification value of 187.02 showing that it has the maximum amount of triacyl glycerols when compared to other oils (olive, almond, coconut, sesame, and sunflower) used in this study.

Acid Value

The amount in mg of KOH required to neutralize the free fatty acids present in 1 g of fat or oil is called the acid value. The acid value depends on the number of free fatty acids. Greater the number of free fatty acids in oil, greater will be the acid value of that oil and vice versa [10].

This study showed that olive oil has the highest acid value of 1.361 as presented in Table-4 indicating that it contains the maximum amount of free fatty acids among the other oils. While sunflower oil has the minimum acid value of 0.263 owing to the minimum amount of fatty acids, paraffin oil, a mineral oil, containing trace amount of fatty acids has a value of 0.224.

pH Value

pH value of the oils indicates their acidic or basic behaviour. Most of the oils are acidic in nature because oils contain fatty acids (Table-6).

Table-6: Acidity classification of materials.

	pH	Characterizatics
I	< 2	Strong Acidic
II	4-2	Acidic
III	7-5	Weak Acidic
IV	7	Neutral
V	7-9	Weak Basic
VI	9-11	Basic
VII	> 11	Strong Basic

As demonstrated in Table-4 all the oils investigated in this study have acidic character. Castor oil is the least acidic among the other oils and has the pH value of 4.92, while cotton seed oil is the most acidic having the pH value of 3.64. The pH value of castor oil is the highest (4.92).

Specific Gravity

Specific gravity is the ratio of the density of a substance to the density of water or the ratio of mass of a substance to the mass of an equal amount of water at specific temperature. Density is the derived quantity since it combines the units of mass and volume and is defined as the mass per unit volume at a fixed temperature [11].

Table-4 shows that the specific gravity of paraffin oil is the higest among all the oils studied and was found to be 0.9999 while that of coconut oil had the minimum specific gravity of 0.9138. This reflects that molecules of paraffin oil are more closely packed and the molecules of coconut oil are loosely packed.

Experimental

Material

The chemicals (ethanol, ether, ethylene glycol, sodium hydroxide, potassium hydroxide and hydrochloric acid) were the products of Merck, Germany while phenolphthalein indicator used was purchased from Sigma Chemical Industries. Distilled water was prepared in the laboratories of Faculty of Pharmacy & Alternative Medicines, The Islamia University of Bahawalpur.

Methods

Characterization of Oils

Cosmetic oils, like all cosmetic ingredients, must be subjected to a comprehensive evaluation. The evaluation criteria include the effect of physicochemical properties on the colloid chemistry and the sensory properties of emulsions. Some basic properties were defined which influence the colloid chemistry as well as sensory characteristics of the emulsion preparations [9] and physicochemical characteristics were determined in this study [6].

Rheology

The method proposed by Li Meijing *et al.* [12] was used to measure the rheological properties of oils. The rheological tests like viscosity measurement, Newtonian and Non-Newtonian behaviour determination of oils were performed using a Brookfield RVDV III Ultra Rheometer with cylindrical spindle and ultra low (UL) adapter. Cylindrical spindle geometry was chosen due to the significantly wider range of shear rates and viscosities that could be measured. The UL adapter was used for low viscosity measurements. Shear rate was varied by adjusting the rate of spindle rotation. Instrument calibration was checked using nominally 990 mPas.s standards purchased from Brookfield. The effect of temperature on the viscosity of different oils was determined between the range of 20-30 °C by using the Brookfield TC-502 circulating bath. Newtonian and Non-Newtonian behaviours of oils were also determined at constant (25 ± 0.1 °C) temperature [12].

Spreadability

The method proposed by Roehl and Brand [8] was used to test the spreadability of the oil using glass plates coated with gelatin. 1 % aqueous solution of gelatin was prepared by gentle heating. Microscopic slides which have a flat, glass surface were wetted uniformly with the gelatin solution. The film was allowed to solidify on a tray floating on an ice bath for 1 hour. The film was then dried at room temperature for two days, followed by storage at 25 °C, dust-free cabin for 24 hours. The spreadability tests were performed in a conditioned room of 52 % relative humidity and 23 °C temperature. Coated glass plates were placed on a milimeter graph paper on a flat surface. 10 μL of the oil to be tested was put on a plate using a microliter pipette. After 5 minutes, the diameter of the circular spreading area was read. The test was repeated 3 times and the mean values were assigned to the given standards [6].

Pour Point and Cloud Point

The determination of pour and cloud points were performed in a water bath (± 0.1 °C). 15 mL of oil was put into the test tube which was placed in the water bath. The temperature of the water bath at 20 °C was decreased gradually by 0.5 °C each time and the point where clouding appeared was noted. Again, the temperature of the water bath was decreased and the point at which the oil solidified was noted. Each test was repeated three times.

The methods proposed by U.G. Akpan *et al.* [13] were used to determine the saponification value, acid value, pH and density of oils.

Determination of Saponification Value

Indicator method was used to determine the saponification value. 2 g samples were weighed into a conical flask, 25 mL of 0.1 N ethanolic potassium hydroxide was then added. The contents of which were constantly stirred and allowed to boil gently for 60 min. A reflux condenser was placed on the flask. Few drops of phenolphthalein indicator were added to the warm solution and then titrated with 0.5 M HCl to the end point until the pink colour of the indicator disappeared. The same procedure was used for other samples and the blank. The expression for saponification value (SV) is given by: $SV = 56.1\ N (V_o-V_1)/M$, where V_o = volume of the solution used for blank test; V_1 = volume of the solution used for determination; N = Actual normality of HCl used; M = Mass of the sample.

Determination of Acid Value

25 mL of diethyl ether and 25 mL of ethanol were mixed in a 250 mL beaker. The resulting mixture was added to 10 g of oil in a 250 mL conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1 M NaOH with constant shaking to the end point where a dark pink colour was observed and the volume of 0.1 M NaOH (V_o) was noted. Free Fatty Acid (FFA) was calculated from: $V_o/W_o \times 28.3 \times 100$.

Determination of pH Value

2 g of the sample was poured into a clean, dry 25 mL beaker and 13 mL of hot (70 ± 3 °C)

distilled water was added and stirred slowly. The mixture was then cooled in a cold-water bath to 25 °C. The pH electrode was standardized with buffer solution, before the pH values were recorded.

Determination of Specific Gravity

Density bottle was used to determine the density of oils. A clean and dry bottle of 25 mL capacity was weighed (W_o) and then filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing drying process and weighed to give (W_2). The expression for specific gravity (Spgr) is: Spgr = $(W_1-W_o)/(W_2-W_o)$ = Mass of the substance / Mass of an equal volume of water.

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