Surface Phenomena of Fats for Parenteral Nutrition[1]

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THERE are many investigators vitally concerned with the physiological responses inherent in the parenteral administration of fat emulsions. Many oils and emulsifiers mixed in various proportions have been used, with varying degrees of success. However the fundamental problems, concerning thermogenic responses occasioned at times following the use of fatty emulsions, emusification of oils, and stability of the emulsions, still remain. The physical properties of the oils used in preparing emulsions for intravenous use seem to have received the least amount of investigative effort since the oils apparently have been selected at random in most cases. Because of the intensive effort on the part of many investigators in the preparation and clinical testing of fat emulsions, the need has arisen for the systematic physicochemical investigation of some available synthetic fats and vegetable oils of known origin and processing conditions, which might be suitable for use in emulsions. Most of these oils are being clinically tested.

It would seem that some of the variable properties of good prime oils, of comparable history and processing conditions, are the surface phenomena characteristic of these materials. With given amounts of emulsifying agent and water it is theoretically possible that different oils will be capable of being emulsified to different degrees or extents. According to Harkins and Zollman (2), an interfacial tension below 10 dynes cm^{-1} permits easy emulsification, and spontaneous emulsification occurs below an interfacial tension of 1 dyne cm^{-1}. Since the interfacial tension of a liquid is a meaure of its free surface energy per square centimeter of interface, determination of interfacial tension should therefore provide information as to ease of emulsifiability.

Literature references (3-7) with respect to the surface tensions and interfacial tensions of vegetable oils seldom report the characteristics of the oil (*i.e.*, source, processing conditions, free fatty acids, degree of refining, etc.), which can profoundly affect the surface properties. Therefore various fats most of which have been made available to interested physiologists for utilization as emulsifiable products, have been investigated to determine their surface phenomena. This information can be related to their properties in emulsions.

Materials

The fatty materials whose surface and interfacial tensions have been measured included both natural vegetable oils and two synthetic fats.

The natural vegetable oils were produced by conventional mechanical pressing or solvent-extraction (8). The pressed oils included peanut oil, cottonseed oil, coconut oil, pecan oil, and olive oil. Another peanut oil was obtained from U. S. No. 1 grade edible peanuts of the Spanish variety, which were flaked and pressed under conditions of maximum cleanliness in pilot-plant equipment with no precooking treatment. (Commercial methods of oil expression invariably involve a cooking period.) Of all the oils used, only this peanut oil was not obtained commercially. Virgin olive oil obtained from California olives was known to be authentic and unadulterated.

Rice oil, obtained from the bran of freshly milled rice, sesame oil, and a peanut oil which was extracted from previously pressed peanut cake were the solvent-extracted oils. Of the natural oils, all except coconut oil were obtained in the crude, or unrefined, state.

One of the synthetic fats was made up to resemble somewhat the composition of human depot fat, with a fatty acid composition of approximately 60% oleic, 30% palmitic, 8% stearic, and 2% linoleic (low). It was made by the esterification of glycerol with the corresponding free fatty acids.

The second synthetic fat was 1,3-dipalmito-2-lactin, which was made from 1,3-dipalmitin and 0-benzyl lactyl chloride and subsequent hydrogenolysis (9).

All of the oils, with the exception of commercially refined coconut oil, were alkali-refined, bleached, and deodorized in stainless steel or glass laboratory equipment, and maintained under an atmosphere of inert gas. The refining, bleaching, and analytical procedures followed the official methods of the American Oil Chemists' Society (10). The oils were deodorized in equipment described by Bailey and Feuge (11). Analytical data are included in Table I.

The peroxide value of the fully processed oils was 0.0.

TABLE I

Analytical Data on Oils

Type of oil	Free fatty acid, percent	Wijs iodine value	Unsaponifiable matter, percent	Phosphorous, percentage $\times 10^{-5}$
Peanut, crude, cold-pressed	0.20	......	0.72	18.0
Peanut, refined, cold-pressed	0.005	93.9	0.36	0.04
Peanut, crude, screw-pressed	2.50	......	0.60	1160.00
Peanut, refined, screw-pressed	0.05	94.8	0.32	25.0
Peanut, crude, solvent-extracted	3.40	......	0.30	......
Peanut, refined, solvent-extracted	0.06	96.0	0.52	0.00
Cottonseed, crude, screw-pressed	1.80	......	1.09	......
Cottonseed, refined, screw-pressed	0.01	104.3	0.50	0.60
Sesame, crude, solvent-extracted	0.91	......	......	......
Sesame, refined, solvent-extracted	0.07	116.6	1.50	23.00
Rice, crude, solvent-extracted	0.85	......	......	......
Rice, refined, solvent-extracted	0.06	103.7	1.80	12.00
Coconut, refined, screw-pressed	0.04	8.5	0.16	......
Virgin olive oil, crude, screw-pressed	1.40	85.1	......	......
Virgin olive oil, refined, screw-pressed	0.03	85.2	0.9	37.00
Pecan, crude, screw-pressed	0.40	......	......	......

Method

Determination of the surface tension against air and interfacial tension against water was by a modification of the capillary rise method first proposed by Ferguson (12). The method was later modified again by Ferguson and Kennedy (13), and more recently by Nevin *et al.* (14).

In order to check the precision and accuracy of the apparatus and method, the surface tension of triple-distilled water was determined at several tempera-

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tures and found to be within ± 0.08 dyne cm^{-1} of the values reported by Harkins and Brown (15).

In order to check the values of interfacial tension obtained by the present method, the interfacial tension against water of olive oil was compared with published values obtained by different methods. The reported value of the interfacial tension of olive oil as determined by the capillary rise method is the same as given in the present report (16), and that obtained by the drop weight method is 1 dyne cm^{-1} higher (3).

When the column of liquid in the capillary tube used in the measurements was oil-water-oil, the value was the same as that obtained when only oil was in the capillary tube. This proves that the forces due to the interfacial tensions at the two water-oil interfaces in the horizontal tube were acting in opposite directions and were of the same magnitude. This is another indication that the method used in the present investigation was satisfactory.

Results

From experimental data, the surface tensions of the various oils at several temperatures were calculated, and the values obtained were plotted as functions of temperature as shown in Figure 1. In each case the surface tension varied linearly with the temperature. The method of Least Squares was applied to the experimental data, and equations were developed by means of which the surface tension of each oil can be calculated at any temperature over the range 25°-75°. These equations are given in Table II.

The interfacial tensions against water of the oils at 25° are also included in Table II.

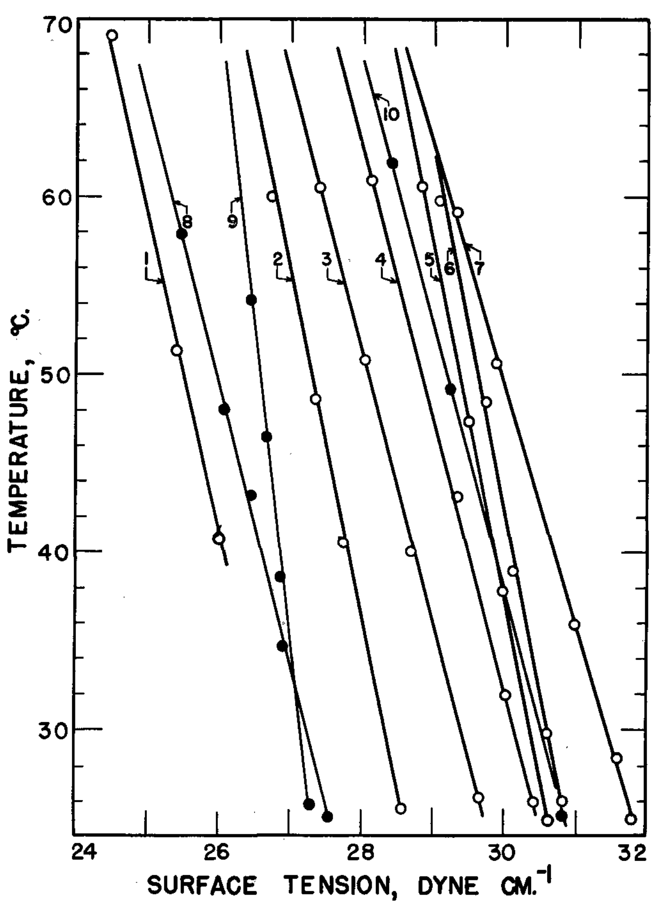

FIG. 1. Surface tensions of the natural oils as functions of temperature. Refined oils—1, coconut; 2, olive; 3, sesame; 4, cold-pressed peanut; 5. rice; 6, cottonseed; 7, pre-pressed peanut. Crude oils—8, cold-pressed peanut; 9, cottonseed; 10, olive.

TABLE II

Surface Tension Equations and Interfacial Tensions Against Water

Type of oil	Least Square equations,[b] γ dyne cm^{-1} t°C.	Interfacial tension, 25°C. dyne cm^{-1}
Peanut, crude, cold-pressed	$\gamma = -0.06174t + 29.06$	19.9
Peanut, purified, cold-pressed	$\gamma = -0.06368t + 32.00$	22.9
Peanut, purified, screw-pressed	$\gamma = -0.07534t + 33.61$	18.1
Peanut, solvent-extracted, purified	$\gamma = -0.05985t + 31.94$	18.5
Cottonseed, crude, screw-pressed	$\gamma = -0.02833t + 27.99$	1.6
Cottonseed, purified, screw-pressed	$\gamma = -0.04640t + 31.98$	14.9
Olive oil, crude, screw-pressed	$\gamma = -0.06790t + 32.55$	6.3
Olive oil, purified, screw-pressed	$\gamma = -0.04918t + 29.78$	17.6
Coconut, purified, screw-pressed	$\gamma = -0.05990t + 28.49$	12.8
Rice bran, solvent-extracted, crude[a]	....	9.3
Rice bran, solvent extracted, purified	$\gamma = -0.04744t + 31.69$	16.3
Sesame, solvent-extracted, purified	$\gamma = -0.06407t + 31.30$	17.7
Pecan, crude, screw-pressed	$\gamma = -0.06790t + 30.15$	14.2

[a] $\gamma = 29.5$ dyne cm^{-1} at 25°. Values not reproducible after heating.
[b] From 25° to 75°.

One of the synthetic fats, 1,3-dipalmito-2-lactin, had a surface tension of 18.9 dynes cm^{-1} and an interfacial tension against water of 14.8 dynes cm^{-1} at 75°. The other synthetic fat, resembling human depot fat, had a surface tension of 27.3 dynes cm^{-1} and an interfacial tension against water of 18.6 dynes cm^{-1} at 55°.

Discussion

The surface tensions of all the oils were found to decrease with increasing temperature. The spread in surface tension values of the refined oils was about 4.5 dynes cm^{-1}. For example, at the 25° isotherm, the surface tensions of coconut oil (lowest value) and commercial peanut oil (highest value) were 27.0 and 31.5 dynes cm^{-1}, respectively. The surface tension of olive oil was about midway of the range, and the other oils had surface tensions between 29.0 and 31.5 dynes cm^{-1}. If the coconut oil is excluded, the variation in surface tension values of the other oils is only about 2.5 dynes cm^{-1}.

Surface tensions of the crude oils were in the same range with those of the refined oils. With the exception of olive oil, the surface tension of the crude oil was lower than that of the corresponding refined oil.

The spread of values obtained for the interfacial tensions at 25° of the refined oils was considerably wider than that of the surface tensions, namely 9 dynes cm^{-1}. Coconut oil again was the lowest with an interfacial tension of 12.8 dynes cm^{-1}, and the refined, cold pressed peanut oil had the highest interfacial tension of 22.9 dynes cm^{-1}. The order of the oils with increasing interfacial tension values was not the same as it was with increasing surface tension values.

The representative crude oils had much lower interfacial tensions than did the refined oils. Cottonseed, rice, and olive oils were particularly low in this property. In fact, the cottonseed and rice oils contained some constituents which gave rise to apparent solubility across the oil-water interface, thereby causing the interfacial tension value to change with time. Crude cottonseed and rice oils gave instantaneous "negative" interfacial tension values (*i.e.*, a reversal of the meniscus of the water phase), which on standing increased to give a maximum positive value. This is an important phenomenon. According to King and Mukherjee (16), emulsion stability is related to change in the area of the interface with time.

Crude rice oil was found to be effective in lowering the interfacial tension of a refined oil, when admixed with the latter. For example, refined and bleached olive oil had an interfacial tension of 17.6 dynes cm^{-1} at 25°. On adding 2% of crude rice oil, the interfacial tension was lowered to 8.1 dynes cm^{-1}, and 11% of crude rice oil lowered the value to 6.3 dynes cm^{-1}.

The difference in interfacial tensions of a crude oil and the corresponding refined oil apparently is due to some material which is removed by the normal refining procedure. That this material is not completely in the unsaponifiable matter was determined by concentrating the unsaponifiable matter of olive oil and adding this material back to refined cottonseed and olive oils, as indicated in Table III.

TABLE III
Surface and Interfacial Tensions at 25° of Refined Oils Containing Added Unsaponifiable Matter

Unsaponifiables, weight percentage	Refined cottonseed oil		Refined olive oil	
	Surface tension, dyne cm^{-1}	Interfacial tension, dyne cm^{-1}	Surface tension, dyne cm^{-1}	Interfacial tension, dyne cm^{-1}
0	30.8	14.9	28.6	17.6
2	31.2	17.9	29.5	20.5
4	30.0	15.5	27.6	18.0
10	25.3	11.9	25.3	12.9

It can be seen that there was an initial rise in the surface and interfacial tension values of both oils, followed by a decrease as the content of unsaponifiable matter was increased. It might be mentioned that 10% by weight of unsaponifiable matter represents at least a ten-fold increase over the amount naturally present in vegetable oils.

On the basis of surface phenomena alone, the crude oils investigated should be more easily emulsified than the refined oils if no added emulsifiers are used. What the effects of the non-glycerides in the crude oils would be, physiologically, is another matter. However the addition of very small amounts of emulsifying agents to the refined oils, as indicated, is sufficient to lower their interfacial tensions to the easily emulsifiable range.

Summary

Surface tensions of natural vegetable oils of known origin and processing conditions have been measured over the temperature range 25°-27° by means of a modification of the capillary rise method. Interfacial tensions against water of the crude and refined oils have been determined at 25°. The surface tensions and interfacial tensions against water of 1,3-dipalmito-2-lactin at 75° and of a synthetic fat at 55° have been determined.

The method of Least Squares was applied to the surface tension-temperature data to obtain equations of the form, $\gamma = a - bt$, where γ is the surface tension in dynes cm^{-1}, t is the temperature in °C., and a and b are the least square factors.

Only the crude rice, olive, and cottonseed oils have interfacial tensions against water less than 10 dynes cm^{-1}. Of the refined oils, coconut oil has the lowest interfacial tension, namely 12.8 dynes cm^{-1}. All of the other refined oils have interfacial tensions between 14.5 and 22.9 dynes cm^{-1} at 25°. The addition of unsaponifiable matter to a refined oil had little effect on its interfacial tension, but the addition of a small percentage of a crude oil to a refined oil lowered the interfacial tension of the refined oil considerably.

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Solvent Extraction of Meat Offal

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THE application of solvent extraction to the removal of oil from vegetable oil seeds has been extensively investigated by many, but this application has not been reported for meat offal. Similarly, the use of the Iowa State College extractor for the extraction of soybeans, cottonseed, and other vegetable oil seeds has been reported by Arnold and coworkers (4, 6). It was considered a natural extension of the work with this extractor to determine the effects of the various operating variables on the extraction of an animal material as meat offal both in the laboratory and in the pilot plant.

The material used in these studies was meat and bone scrap[2] which is produced from the wastes of the meat packing industry. This material, after having been passed through a hogger, had been dry-cooked to coagulate the protein of the meat and to reduce moisture content. The meat and bone scrap contained

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