Surface Active Properties of Sulfonated Isoricinoleic Acid

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A new anionic surfactant, sulfonated isoricinoleic acid, was prepared by sulfonation of isoricinoleic acid. Surface active properties, such as surface tension, interfacial tension, emulsifiability, dispersibility and foaming power of sulfonated isoricinoleic acid (SIRA), and sulfonated castor oil or turkey red oil (TRO) were studied and compared. The comparative studies showed that SIRA is a better surface active agent than TRO.

The present work was done because castor oil (consisting mainly of triricinolein) has been thoroughly investigated for preparing various industrially important derivatives, including turkey red oil (TRO) (1), but *Wrightia* oils (rich in isoricinoleic acid) (2–4) have not yet acquired commercial status due to the lack of experimentation and availability. The long term outlook for natural oils and fats is excellent from a supply point of view, due to dramatic productivity improvements throughout the 1980's. These improvements may generate improved yields of oils and fats. Future demand for natural oils and fats should remain relatively stable, and this market will thus be softer than the petroleum market. Keeping this in view, oils and fats (more specifically, *Wrightia* oils) should be thoroughly explored for the preparation of surfactants. Therefore, the present investigation deals with the preparation of sulfonated isoricinoleic acid (SIRA) and TRO. On comparison, we have found the surface active properties of SIRA superior to those of TRO.

EXPERIMENTAL PROCEDURES

General. Infrared spectra were obtained with a Spectromom-2000 (BUDAPEST, Budapest, Hungary). Thin-layer chromatography (TLC) was performed on silica gel "G" coated plates using the solvent combination of petroleum ether/diethyl ether/acetic acid (60:40:2,v/v/v).

Materials. Castor oil was purchased from the local market. *Wrightia tinctoria* seeds were procured from Aligarh market, Uttar Pradesh, India. The oil was Soxhlet extracted from *Wrightia* seeds with n-hexane. The extracted oil (10 g) was saponified using 3 g of potassium hydroxide and 100 ml of alcohol. The soaps were hydrolyzed with dilute hydrochloric acid, and then the liberated fatty acids were repeatedly extracted with diethyl ether. Finally, isoricinoleic acid from total mixed fatty acids was derived following the procedure of Gunstone (5). The purity of the acid was checked by TLC, which showed a single spot in various solvents.

Sulfonation. A typical sulfonation procedure (6) of isoricinoleic acid and castor oil is as follows: 5.54 1 g of isoricinoleic acid was placed in a 100 ml beaker. Concentrated sulfuric acid (2.752 g) was slowly added dropwise from a burette with magnetic stirring over a period of 3 hr. During the addition of sulfuric acid, the temperature was maintained in the range 30–35°C. Stirring was continued for 1 hr, and then the reaction mass was left overnight to complete the reaction. The next day the reaction mixture was washed repeatedly with saturated brine solution and then with caustic soda to the extent of 2% by weight that was added in a 50% aqueous solution.

Analysis. Analysis of SIRA and TRO have been carried out according to the standard procedures of the ISI Indian Standard Specification (7), which are detailed in the rest of this section.

Degree of sulfonation. The procedure of this determination includes the determination of alkalinity of the material and increase in acidity when the material is boiled with dilute sulfuric acid. For the former determination, 10 g of material was dissolved in 100 ml water, and after adding 30 g of NaCl and 25 ml of diethyl ether, it was titrated against standard sulfuric acid, using methyl orange as an indicator. For the determination of the latter, 10 g of material was boiled with 25 ml excess of diluted sulfuric acid on a sand bath for 1½ hr. Then the material was titrated with standard sodium hydroxide solution after adding 30 g NaCl and 25 ml diethyl ether, using methyl orange as an indicator. A simultaneous blank determination was carried out.

Determination of total fatty matter. The solution after the determination of combined acidity was hydrolyzed with dilute sulfuric acid and the fatty matter extracted with diethyl ether, and the solvent was evaporated and then weighed.

Determination of unsulfonated oil/unsulfonated acid. Ten g of material was dissolved in 10 ml of 80% ethanol. Hydrochloric acid was added until the aqueous layer was distinctly acidic to litmus paper. The solution was then extracted with diethyl ether and weighed after ether evaporation.

Determination of calcium soap dispersion value. Twenty ml of 2.30% (W/V) sodium oleate solution was placed in a stoppered conical flask. Two ml of 5% (W/V) sample solution and 25 ml of 0.34% (W/V) calcium chloride solution was added. After shaking the mixture and allowing it to set for 5 min, it was filtered through a bed of glass wool and Gooch aesbestos. The precipitates were washed three times with water, and then the combined washings and filterate were titrated against 0.1 N HCl (A), using a mixed indicator of equal parts by volume of aqueous solutions of methyl orange 0.2% (W/V) and xylene cyanol FF 0.2% (W/V) until a grey color appeared. A blank determination (B) was also carried out. Free alkalinity (C) of 2 ml of 5% (W/V) sample solution, diluted with 75 ml water was also determined using mixed indicator of xylene cyanol FF and methyl orange. Results are expressed as A-B-C.

Surface active properties. Emulsifying power (8). Surface tension of TRO and SIRA was determined by du Nouy's tensiometer (ring detachment method). Interfacial tension between solution of TRO and SIRA

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and light liquid paraffin were also determined with the tensiometer.

Dispersing power (9). Various volumes (40, 80, 120 and 160 ml) of 2.5% (W/V) solutions of SIRA and TRO were added to graduated cylinders. Four g of carbon black and 5 ml of white oil was added to each of these cylinders. Water was added up to a volume of 200 ml. The cylinders were stoppered and tilted 10 times clockwise and counter-clockwise, and then kept stationary.

After periods of 1, 2, 5 and 24 hr, 5 ml of solutions were pipetted out from the center of the cylinders and placed in a petri dish. The water in the samples was evaporated and the petri dishes were reweighed to determine the amount of dispersed carbon.

Foaming power (10). Twenty ml of TRO and SIRA solutions (1.0% W/V) were placed in a 100 ml measuring cylinder provided with a glass stopper. The cylinder was inverted and restored 60 times in two min. Foam volume was noted.

Thirty ml of 2% (W/V) sample solution was placed in another measuring cylinder and then was shaken as described above, and foam volume was noted after different intervals of time.

RESULTS AND DISCUSSION

Results of analyses of TRO and SIRA are shown in Table 1. The degree of sulfonation, total fatty matter (TFM) and calcium soap dispersion values are more pronounced in the case of SIRA than of TRO. On the other hand, TRO has more unsulfonated matter.

Figures 1 and 2 show relative emulsifying powers in terms of surface tension and interfacial tension, respectively. From the graphs it is clear that surface tension and interfacial tension decreases with increases in their concentration. Surface tension and interfacial tension of TRO are found to be more pronounced than those of SIRA above concentrations of 0.10% and 0.15%, respectively. This clearly demonstrates that SIRA is a better emulsifying agent than TRO.

Figures 3, 4, 5 and 6 show relative dispersing powers of TRO and SIRA at 1, 2, 5 and 24 hr time, respectively. From these graphs it is clear that SIRA is a better dispersing agent than TRO, and for a given concentration the dispersing power of SIRA is also greater than TRO. It also appears from the graphs that the dispersing power increases more rapidly in the initial stages than in later stages for a given increase in concentration.

TABLE 1

Sr. no.	Test	Results SIRA	 TRO
1.	Percentage organically combined SO_3	12.88	10.88
	(a) Alkalinity	0.49	0.44
	(b) Combined acidity	1.12	0.92
2.	Degree of sulfonation	16.47	15.39
3.	Total fatty matter (%)	78.2	70.68
4.	Unsulfonated matter (%)	31.3	34.1
5.	Calcium soap dispersion value	1.10	0.95

Figures 7 and 8 demonstrate the variability in the relative foaming power. For a given concentration, the volume of foam produced is larger in SIRA than in TRO. The rate of foam decay is greater in case of TRO, indicating that SIRA has more foaming power than TRO.

With the growing interest in the preparation of surfactants from natural oils and fats, TRO has been used successfully as a wetting agent. In the present investigation based on the above experiments on SIRA, it might be expected that SIRA could also be used alternatively as a better wetting agent than TRO, if some more tests are made to prove its utility in the surfactant industry. Further work is underway to identify the individual products formed in the sulfonation

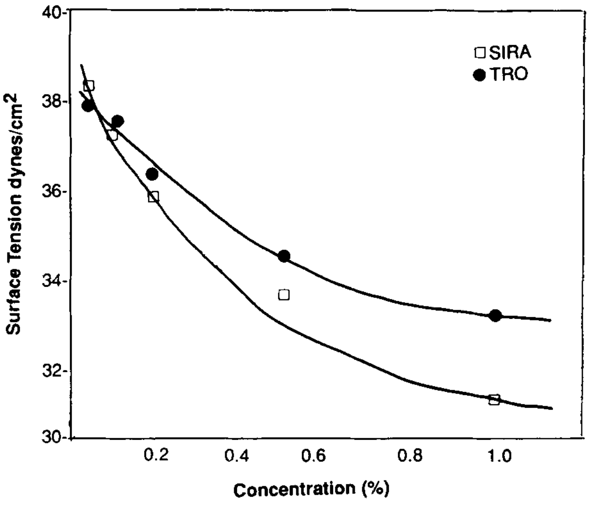

FIG. 1. Surface activity of TRO and SIRA in terms of surface tension.

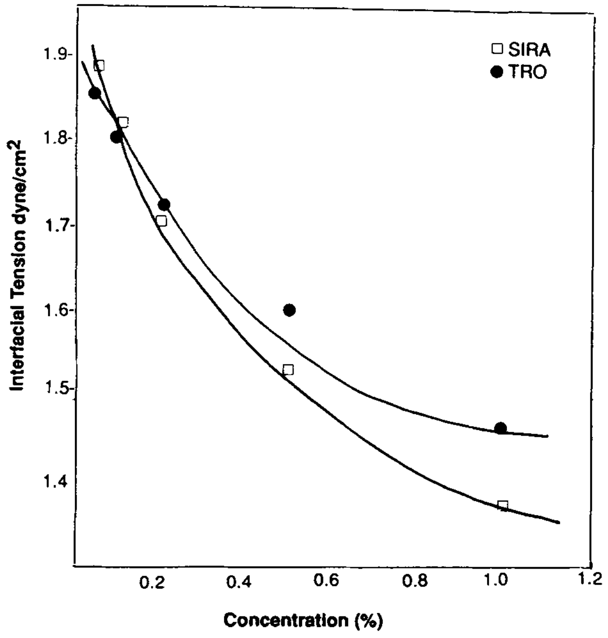

FIG. 2. Surface activity of TRO and SIRA in terms of interfacial tension.

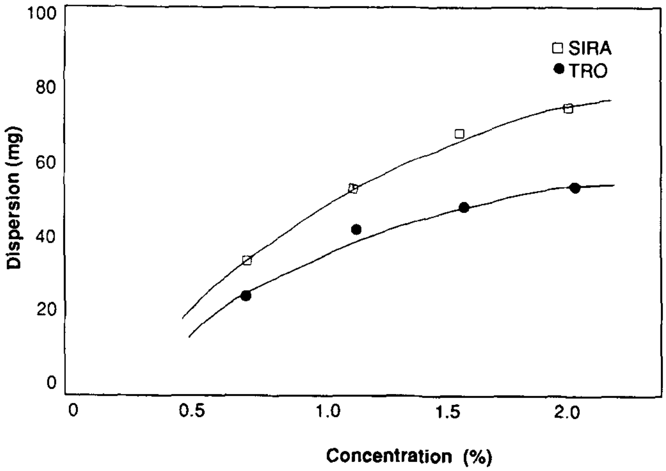

FIG. 3. Relative dispersing power after one hour.

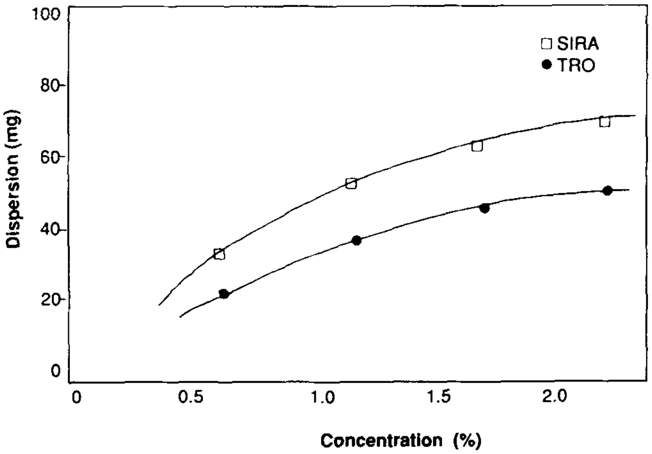

FIG. 4. Relative dispersing power after two hours.

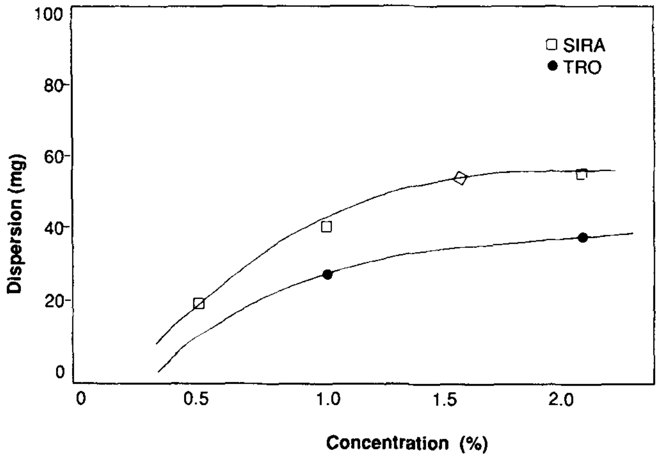

FIG. 5. Relative dispersing power after five hours.

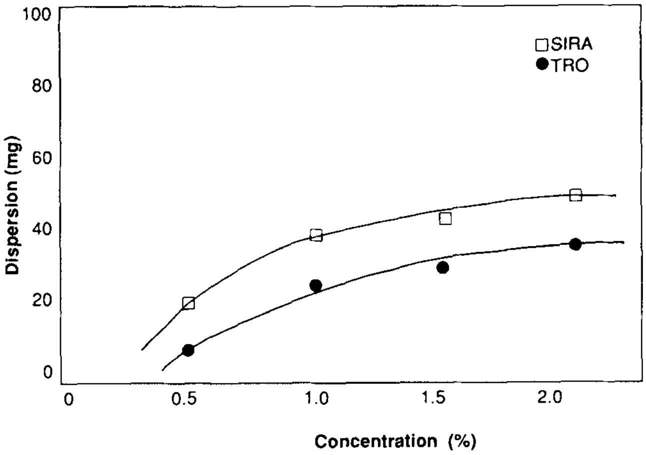

FIG. 6. Relative dispersing power after 24 hours.

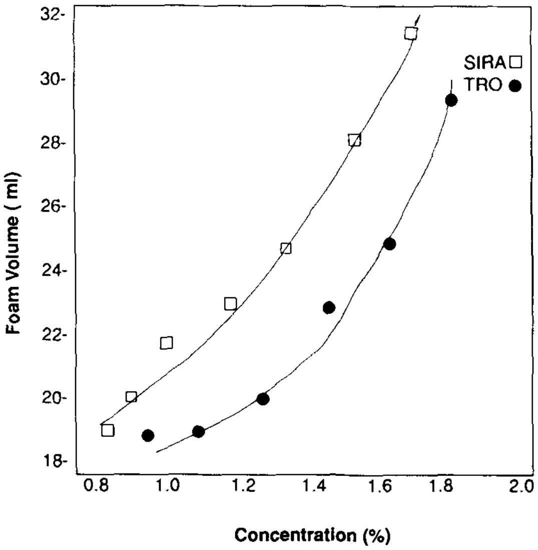

FIG. 7. Relative foaming power in terms of foam value.

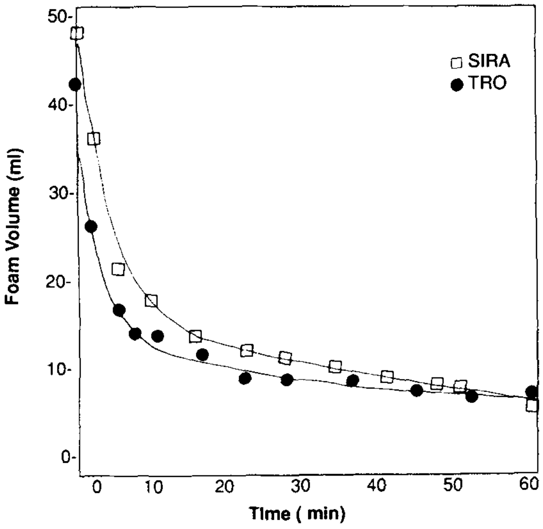

FIG. 8. Foaming power in terms of foam decay.

of isoricinoleic acid as well as to study the wetting properties of this product.

ACKNOWLEDGMENTS

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