

neutralization likewise gave a product probably containing a sodium ester sulfate on the hydrophilic hydroxyl and a sodium sulfonate (IX) on the hydrophobic unsaturate. The phenyl (X) and naphthyl urethanes (XI) as well as the benzoate (XII) and 3, 5 dinitrobenzoate (XIII) derivatives were synthesized according to the procedures given in Shriner and Fuson (6). Additional ethenoxy units were added by further condensation of I with ethylene oxide gas in the presence of a small amount of potassium hydroxide catalyst until a total of 33 (XIV), 43 (XV), and 57 (XVI) moles of ethylene oxide had been introduced into the molecule.

The detergency tests on all of these substances were carried out according to the method of Vaughn and Suter (7), using a launderometer. In each case a test mixture was prepared, using 20% by weight of the derivative, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethylcellulose. All results were compared to an arbitrary standard, taken as 100% and consisting of the above alkaline builders and 20% of the starting material I. Detergency tests were carried out on 0.25 g. of each test mixture in 100 ml. of water. The results of these tests carried out at 140°F. are shown in Table I.

Effect of Various Substituents on Detergency

From the results in Table I it would seem that, in general, the introduction of substituents either to the hydrophobic or hydrophilic portion of the molecule reduces the effectiveness of the product from the detergency standpoint. The chlorinated derivative (II) and the 3,5 dinitrobenzoate (XIII), on the other hand, seemingly possess slightly higher activity than the parent polyethenoxy tallate (I). Very marked lowering in detergency was noted with those products VIII and IX where the substituents groups had presumably entered into both ends of the molecule.

In particular, the introduction of anionic groups into a nonionic detergent is deleterious. Ozonolysis of the hydrophobic groups with probable rupture of the molecule likewise produces an undesirable effect.

TABLE I

Detergency Values of Built Nonionic Tall Oil Derivatives

Derivatives of Polyethenoxy Tallate (13)		Detergency Values			
		Whiteness Retention		Soil Removal	
		Hard Water ^a	Soft Water	Hard Water ^a	Soft Water
I. Polyethenoxy Tallate (13)	A	100	100	100	100
II. Chlorinated	A	103	104	100	100
III. Brominated	A	94	103	100	99
IV. Ozonide	A	75	74	86	90
V. Hydroxy-Formoxy	A	97	110	95	97
VI. Hydroxy-Acetoxy	A	91	104	96	96
VII. Maleic Anhydride Adduct	A	85	100	94	97
VIII. Excessively Chlorinated	A-B	57	66	63	76
IX. Sodium Sulfonate	A-B	65	64	77	97
X. Phenyl Urethane	B	98	106	96	95
XI. Naphthyl Urethane	B	98	107	76	85
XII. Benzoate	B	91	99	92	94
XIII. 3,5 Dinitrobenzoate	B	112	103	98	99
XIV. Polyethenoxy Tallate (33)	B	106	101	99	100
XV. Polyethenoxy Tallate (43)	B	105	101	97	98
XVI. Polyethenoxy Tallate (57)	B	103	100	95	96

^a 252 p.p.m. hardness.

A. Derivative of the hydrophobic double bond
 B. Derivative of the hydrophilic hydroxyl group
 A-B. Probable derivative of both groups

Extension of the polyethenoxy chain to 57 ethenoxy units decreased soil removal values of the products slightly but did not adversely affect the whiteness retention. This is not in accord with previous results on the short chain acids (2), which showed a marked drop in detergency with increasing ethenoxy chain. It should be emphasized that the experimental error in the detergency tests may be as high as $\pm 3\%$ so that, *e. g.*, detergency values of 98 or 102% should in all probability be considered equivalent to the standard.

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Densities and Viscosities of Trichloroethylene Miscellas of Cottonseed Oil, Fish Oil, and Beef Tallow

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THE densities and viscosities of soybean oil miscellas for three solvents, hexane, trichloroethylene, and ethylene dichloride, for three temperatures have been reported by Johnstone, Spoor, and Goss (4). The densities of trichloroethylene miscellas of wheat germ oil, cottonseed oil, and milkweed seed oil (2) and of methylene chloride-soybean oil miscellas at 25°C. (1) have been reported previously from this laboratory. The present paper reports data on the densities and viscosities of trichloroethylene miscellas of cottonseed oil, fish oil, and beef tallow for four temperatures.

Experimental Methods

The cottonseed oil was the crude oil produced by the extraction of prime cottonseed by trichloroethylene and had a density of 0.932 g. per cc. at 25°C., an iodine number of 112, and a free fatty acid content of 1.10%. The fish oil was produced by the trichloroethylene extraction of a mixed fish scrap from California¹ and had a density of 0.951 at 25°C. The concentrated miscella direct from the extraction process miscellas used were produced directly by dilution of

¹ Courtesy of Stanley Hiller, San Francisco.

ess rather than from stripped oil. The beef tallow resulted from the trichloroethylene extraction of dry rendered meat and bone scrap. As in the case of the fish oil, concentrated miscella rather than tallow was used in making up the miscellas.

The densities and viscosities of the various miscellas were determined at four temperatures: 25°, 35°, 50°, and 70°C. An Ostwald pipette, with a water constant of 0.0011983 at 25°C., was used for determining viscosities. Densities were determined in 25 cc. pycnometers. A water bath controlled thermostatically to within $\pm 0.02^\circ\text{C}$. was used to maintain desired temperatures.

Results

An examination of the results (Table I) showed that the viscosities in centipoises, μ , is related to the temperature, t , in $^\circ\text{C}$. and the weight fraction of the oil in the mixture, x , by the equation $\log \mu = ax - b$

TABLE I
Densities and Viscosities of Various Fat-Trichloroethylene Miscellas

Miscella Concentration % fat	Viscosity Centipoises				Density Gr. per cc.			
	Temperature $^\circ\text{C}$.				Temperature $^\circ\text{C}$.			
	25	35	50	70	25	35	50	70
Cottonseed Oil								
0.00	0.590	0.543	0.486	0.419	1.456	1.438	1.412	1.379
5.37	0.749	0.682	0.596	0.501	1.413	1.403	1.379	1.350
9.94	0.959	0.856	0.731	0.596	1.379	1.361	1.339	1.308
15.07	1.233	1.092	0.910	0.728	1.341	1.325	1.307	1.280
19.94	1.547	1.353	1.121	0.883	1.306	1.293	1.274	1.250
30.03	2.405	2.053	1.649	1.283	1.248	1.237	1.219	1.200
34.88	2.953	2.482	1.969	1.484	1.208	1.196	1.179	1.157
39.91	3.789	3.140	2.436	1.791	1.187	1.176	1.160	1.139
58.97	8.664	6.793	4.943	3.436	1.096	1.087	1.073	1.056
100.00	63.12	41.40	24.15	12.44	0.932	0.925	0.913	0.902
Fish Oil								
	25	40	55	70	25	40	55	70
0.00	0.603	0.525	0.466	0.416	1.455	1.437	1.400	1.381
2.02	0.648	0.568	0.504	0.443	1.439	1.421	1.390	1.364
8.73	0.916	0.770	0.667	0.563	1.386	1.370	1.344	1.314
14.55	1.240	1.033	0.867	0.718	1.345	1.330	1.300	1.284
18.55	1.550	1.253	1.051	0.864	1.319	1.305	1.280	1.259
25.10	2.082	1.654	1.342	1.090	1.285	1.273	1.250	1.229
29.94	2.715	2.105	1.671	1.364	1.254	1.239	1.222	1.202
40.20	5.188	3.732	2.765	2.153	1.191	1.179	1.165	1.144
Beef Tallow								
	25	40	55	70	25	40	55	70
0.00	0.603	0.525	0.466	0.416	1.455	1.437	1.400	1.381
5.26	0.744	0.645	0.568	0.484	1.411	1.395	1.365	1.342
11.86	0.886	0.818	0.704	0.590	1.368	1.350	1.323	1.300
17.40	1.298	1.065	0.905	0.754	1.321	1.308	1.281	1.259
20.67	1.574	1.265	1.056	0.889	1.294	1.283	1.257	1.233
26.77	2.105	1.595	1.334	1.087	1.253	1.243	1.218	1.198
30.47	2.498	1.888	1.554	1.258	1.231	1.220	1.196	1.175
39.99	3.872	2.731	2.212	1.751	1.172	1.163	1.141	1.125

where a and b are functions of the temperature. Equations for calculating a and b are given in Table II. The general equation applies with an accuracy of $\pm 2\%$ on miscellas containing up to 40% cottonseed oil and with an accuracy of $\pm 4\%$ on miscellas containing up to 30% fish oil or tallow. It is also applicable to the corrected² data of Johnstone, Spoor, and Goss (4) for trichloroethylene-soybean oil miscellas up to 40% oil content with an accuracy of $\pm 2\%$, using the following values: $a = 2.205 - 0.0079t$ and $b = 0.133 + 0.0036t$.

²The viscosity data in this paper were incorrectly calculated and must be corrected by multiplying by the square of the respective densities (3).

TABLE II
Equations for Calculating Viscosities and Densities of Fat-Trichloroethylene Miscellas

Viscosity, centipoises $\log \mu = ax - b$	Density, gr. per cc. $D = mt + n$
Cottonseed Oil	
$a = 2.24 - 0.0094t$	$m = -0.00167 + 0.0021x - 0.0013x^2$
$b = 0.1364 - 0.00353t$	$n = 1.4905 - 0.7543x + 0.1931x^2$
Accuracy $\pm 2\%$, to 40% oil	Accuracy $\pm 1\%$, to 60% oil
Fish Oil	
$a = 2.37 - .0104t$	$m = -0.00167 + 0.0021x - 0.0013x^2$
$b = .133 + .0036t$	$n = 1.4905 - 0.7543x + 0.1931x^2$
Accuracy $\pm 4\%$, to 30% oil	Accuracy $\pm 1\%$, to 40% oil
Beef Tallow	
$a = 2.26 - .0104t$	$m = -0.00167 + 0.0021x - 0.0013x^2$
$b = .133 + .0036t$	$n = 1.4905 - 0.8100x + 0.1931x^2$
Accuracy $\pm 4\%$, to 30% tallow	Accuracy $\pm 1\%$, to 40% tallow

The relation for density is given by $D = mt + n$ where $D =$ density in grams per cc. of m and n given in the tables. The values calculated by the equation have an accuracy of $\pm 1\%$ for miscellas containing up to 60% cottonseed oil and 40% fish oil or tallow. The equation also applies with an accuracy of 1% up to 40% soybean oil to the data of Johnstone, Spoor, and Goss (4).

Discussion

Within the limits of concentration and temperature noted, the equations can be applied with excellent accuracy. Beyond these limits their accuracy is somewhat less but should be sufficient for certain uses. The density equations may be simplified somewhat at the expense of a small amount of accuracy by dropping the x^2 quantity.

Some deviations from the data can result from the use of a fat or oil of the same kind but of slightly different properties resulting from it being derived from a different batch of raw material. This crude cottonseed oil may vary as much as 2% in density. The fish oil and the tallow were extracted from animal wastes which may vary somewhat in composition. In spite of these limitations the data should be satisfactory for most plant design and control purposes.

The toxicity to cattle of certain batches of trichloroethylene-extracted soybean oil meal has raised the question of possible toxicity of other products extracted by trichloroethylene. Since the work presented in this paper was a study in extraction only, the use of trichloroethylene as an experimental solvent should not be construed as a recommendation by the authors that the product resulting from this extraction is or is not suitable as a feed.

Summary

Data on the densities and viscosities of miscellas from trichloroethylene and cottonseed oil, fish oil, and beef tallow for four different temperatures are presented. Equations, with the necessary constants, are given for calculating both densities and viscosities.

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