

The effect of the concentration of the water-soluble component on the rheology of some oil-in-water emulsions containing long-chain alcohols

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The effect of the concentration of two non-ionic water-soluble components—Sorbester Q12 (polyoxyethylene sorbitan monolaurate) and cetomacrogol 1000—and two ionic water-soluble components—cetrimide and sodium lauryl sulphate—on the rheology of some emulsions has been examined. Emulsions containing oleyl and lauryl alcohol exhibited an increase in consistency with increasing surfactant content. Maximum values for static yield value and apparent viscosity were found to occur with cetostearyl alcohol as the oil-soluble component. The values of the rheological parameters for products containing ionic surfactants tended to be higher than for non-ionics, but molal plots (and preliminary studies with Texofor N4, Texofor FX170 and Solumin FX170SD) suggested that this was an effect due to molecular weight rather than charge.

IT has previously been postulated by Talman, Davies & Rowan (1967) that the flow behaviour of a series of oil-in-water emulsions was related to the "intrinsic" strength of a gel formed in the continuous phase by the interaction of oil- and water-soluble components. The present paper is concerned with the effect of water-soluble component concentration on a similar series of emulsions.

Experimental

The general formula used for the preparation of the emulsions was: liquid paraffin, 50.0, oil-soluble component, 0.25 to 10, water-soluble component, 0.125 to 5.0, distilled water to 100.0 g.

The materials and methods given below are additional to those previously described (Talman & others, 1967).

Materials. An ethoxylated alkyl cresol (Texofor FX170), the sodium salt of the corresponding sulphated material (Solumin FX170SD) and an ethoxylated aliphatic alcohol (Texofor N4) [from Glovers (Chemicals) Ltd., Leeds] were used without further purification.

Preparation of gels. The technique adopted was similar to that employed for the emulsions. Since the latter had a phase weight ratio of about 0.5, the concentration of water-soluble component used to prepare a gel was twice that of the corresponding emulsion. All gels contained 10% w/w of the stated alcohol.

Rheological examination. Boylan (1966) has examined a number of pharmaceutical products using a Ferranti-Shirley viscometer and has pointed out some of the difficulties inherent in meaningful interpretation of the rheograms. The spur or abrupt change of slope which was characteristic of the rheograms for which we have reported a static yield value, was replaced in some instances by a more gradual change of slope. For comparative purposes, in the latter case we took the mean of the shear stress range over which the gradual change occurred and quote this as the mean static yield value in Tables 1, 3 and 5.

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Results and discussion

With emulsions containing oleyl alcohol, an increase in the concentration of the water-soluble component generally resulted in the appearance of pseudoplasticity and a rise in apparent viscosity. The latter was more marked in those emulsions containing the higher concentrations of the alcohol in combination with ionic surfactants (Table 1). Oleyl alcohol dispersed in solutions of water-soluble components to give thin milky fluids rather than gels, an exception being 5.0% w/w cetrimide solution. In general, the onset of pseudoplasticity and rise in apparent viscosity cannot therefore be attributed to even weak gel formation. The slight increase in viscosity of the external phase (1 to 3cP for 0.5 to 5.0% w/w cetomacrogol 1000), accentuated by thin film effects in the interglobular spaces and electroviscous phenomena probably account for the observed changes (Sherman, 1964). We found that at constant amounts of water-soluble component the alterations in consistency with increasing oleyl alcohol content were largely due to phase weight ratio effects. Where a gel was formed, as with 5.0% w/w cetrimide, the emulsions containing 8 and 10% w/w oil-soluble component exhibited a mean static yield value.

TABLE 1. EFFECT OF WATER-SOLUBLE COMPONENT CONCENTRATION ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING OLEYL ALCOHOL

Water-soluble component		Oleyl alcohol concentration (% w/w)											
		1		2		4		6		8		10	
	% w/w	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Cetomacrogol 1000	0.5	11	0	16	0	18	0	21	0	25	0	27	0
	1.0	16	0	18	0	21	0	25	0	32	0	34	0
	2.0	18	0	20	0	24	0	30	0	37	0	47	*
	5.0	33	0	37	*	44	*	53	*	64	*	76	*
Sorbester Q12	0.5	10	0	11	0	13	0	15	0	18	0	22	0
	1.0	16	0	15	0	17	0	23	0	25	0	33	*
	2.0	17	0	18	0	20	0	27	0	32	*	39	*
	5.0	24	0	26	0	32	0	36	*	45	*	57	*
Cetrimide	0.5	13	0	11	0	13	0	14	0	20	0	21	0
	1.0	9	0	10	0	14	0	19	0	14	0	33	*
	2.0	9	0	9	0	17	0	29	*	39	*	52	*
	5.0	17	0	19	0	82	*	139	*	180	†1382	228	†1809
Sodium lauryl sulphate	0.5	15	0	11	0	15	0	19	0	23	0	30	0
	1.0	11	0	13	0	17	0	26	0	36	*	46	*
	2.0	6	0	9	0	19	0	32	*	63	*	63	*
	5.0	10	0	8	0	31	*	38	*	74	*	122	*

* Pseudoplastic.

† Mean static yield value.

The data for emulsions containing oleyl and lauryl alcohols, together with cetomacrogol 1000 or Sorbester Q12 as the water-soluble component, were remarkably similar. In contradistinction to oleyl alcohol, lauryl alcohol formed weak gels with both of the foregoing materials and might be expected to yield emulsions of slightly higher consistency than was actually observed. In separate experiments lauryl alcohol dissolved in liquid paraffin was carefully placed on top of solutions containing each of the water-soluble components. On standing at room temperature

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there was no apparent change in those systems containing non-ionic surfactants whereas an amorphous precipitate formed in the aqueous phases containing sodium lauryl sulphate and cetrimide. It is significant that where there was no visible evidence of migration of alcohol from the oil to aqueous phase the emulsions were unexpectedly thin and did not have a static yield value. As may be seen from Table 2, nearly all emulsions containing an ionic material exhibited non-Newtonian flow characteristics; some having a static yield value. Larger amounts of both alcohol and ionic surfactant gave smooth products but the rheograms became so irregular that they could not be interpreted. Such behaviour was also apparent in gels prepared with cetrimide. We tentatively ascribe this irregularity to a large elastic component as has been noted by Pilpel (1966) for related systems.

TABLE 2. EFFECT OF WATER-SOLUBLE COMPONENT CONCENTRATION ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING LAURYL ALCOHOL

Water-soluble component	% w/w	Lauryl alcohol concentration (% w/w)											
		1		2		4		6		8		10	
		η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Cetomacrogol 1000..	0.5	15	0	15	0	16	0	18	0	21	0	28	0
	1.0	16	0	17	0	20	0	24	0	29	0	34	*
	2.0	18	0	20	0	24	0	30	0	36	*	45	*
	5.0	28	0	22	0	46	*	55	*	65	*	83	*
Sorbester Q12	0.5	15	0	15	0	19	0	20	0	23	0	25	0
	1.0	13	0	15	0	17	0	22	0	25	0	31	*
	2.0	16	0	17	0	20	0	27	0	30	*	37	*
	5.0	25	0	27	0	32	0	39	*	43	*	59	*
Cetrimide ..	0.5	39	151	64	352	58	477	74	503	79	691	94	754
	1.0	36	*	88	452	127	302	202	979	249	1432	286	1709
	2.0	23	*	104	427	280	1155	x	x	x	x	x	x
	5.0	14	0	49	*	188	930	x	x	x	x	x	x
Sodium lauryl sulphate ..	0.5	19	63	69	364	105	452	130	565	161	678	198	854
	1.0	20	0	46	*	96	264	118	327	189	754	228	1005
	2.0	24	0	85	352	222	302	287	1357	389	2010	447	2764
	5.0	24	*	37	*	262	603	515	2111	x	x	x	x

* Pseudoplastic.

x Traces uninterpretable.

Sherman (1959) proposed that the emulsifier concentration was related to the viscosity and phase volume by an equation of the general form:

$$\ln \frac{\eta}{\eta_0} = a C \phi + b$$

where η and η_0 are the viscosities of the emulsion and the continuous phase respectively, ϕ the phase volume ratio, a and b are constants and C is the concentration of emulsifier. We applied this equation to our data for all emulsions containing oleyl alcohol and lauryl alcohol with non-ionic surfactants but did not obtain a linear plot for $\ln \eta/\eta_0$ or η/η_0 against C for a constant value of ϕ . This suggested that the relation between the rheological properties and the concentration of water-soluble component was more complex than has been postulated by Sherman. In a later paper he modified the equation to take into account the globule size distribution (Sherman, 1963). For oil-in-water emulsions he found that increasing C caused greater heterogeneity of size distribution and the

formation of multiple phase globules, neither of which have been observed in our systems.

Our results for emulsions containing cetostearyl alcohol and an extended range of water-soluble component concentrations showed maxima in both apparent viscosity (Fig. 1) and static yield value (Fig. 2). These maxima became progressively less marked as the concentration of cetostearyl alcohol was reduced and were not obvious at 0.75 and 0.25% w/w where the products were thin milky fluids (Table 3). These findings

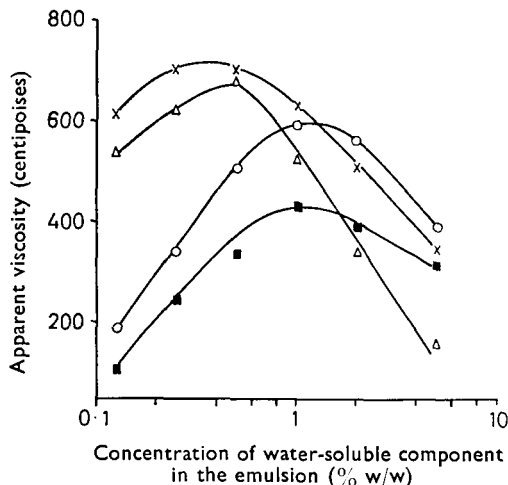


FIG. 1. Effect of water-soluble component concentration (%w/w) on apparent viscosity of emulsions containing 7%w/w cetostearyl alcohol. ■, Sorbester Q12. ○, Cetomacrogol 1000. △, Sodium lauryl sulphate. ×, Cetrimide.

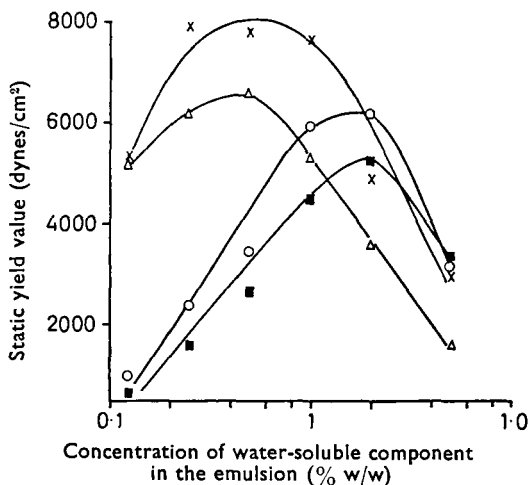


FIG. 2. Effect of water-soluble component concentration (%w/w) on static yield value of emulsions containing 7%w/w cetostearyl alcohol. ■, Sorbester Q12. ○, Cetomacrogol 1000. △, Sodium lauryl sulphate. ×, Cetrimide.

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TABLE 3. EFFECT OF WATER-SOLUBLE COMPONENT CONCENTRATION ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING CETOSTEARYL ALCOHOL

Water-soluble component	% w/w	Cetostearyl alcohol concentration (% w/w)											
		0.25		0.75		1.5		2.5		4.0		7.0	
		η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Cetomacrogol 1000...	0.125	11	0	13	0	60	251	107	553	140	804	188	967
	0.25	10	0	12	0	55	226	156	892	248	1532	341	2362
	0.5	13	0	19	0	61	214	141	980	284	1508	506	3424
	1.0	14	0	15	0	42	*	149	980	340	2713	594	5905
	2.0	15	0	15	0	41	*	82	226	203	1489	562	6159
	5.0	33	0	36	0	63	•	94	151	141	276	393	3015
Sorbester Q12	0.125	10	0	12	0	47	201	58	301	84	502	107	603
	0.25	9	0	11	0	45	226	98	628	130	779	244	1558
	0.5	12	0	13	0	29	126	94	792	176	1407	336	2638
	1.0	8	0	7	0	23	*	50	402	172	1507	430	4522
	2.0	12	0	13	0	25	*	56	427	151	1307	392	5025
	5.0	15	0	19	0	39	*	54	364	117	879	315	3341
Cetrimide	0.125	10	0	11	0	44	125	76	377	206	1557	612	5339
	0.25	10	0	10	0	44	138	98	653	250	2211	701	†7915
	0.5	11	0	15	0	46	251	130	1005	269	2412	701	†7789
	1.0	13	0	18	0	29	75	92	704	182	1658	630	†7664
	2.0	18	0	21	0	28	126	50	452	151	1155	508	4900
	5.0	16	0	20	0	28	0	44	101	87	126	343	2952
Sodium lauryl sulphate	0.125	11	0	10	0	44	126	87	490	153	1206	534	5151
	0.25	12	0	13	0	35	138	139	942	225	1708	617	†6156
	0.5	12	0	18	0	52	251	120	936	269	1885	676	†6533
	1.0	15	0	22	0	32	57	117	949	172	1382	517	†5025
	2.0	26	0	32	0	21	25	50	402	101	817	343	3518
	5.0	13	0	38	0	33	0	37	0	45	0	154	1055

* Pseudoplastic.
† Mean static yield value.

are not in agreement with those of Axon (1956) who reported that the plastic viscosity of emulsions containing cetyl alcohol was directly proportional to the concentration of sodium lauryl sulphate between 0.2

TABLE 4. EFFECT OF WATER-SOLUBLE COMPONENT CONCENTRATION ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF GELS CONTAINING 10% w/w OIL-SOLUBLE COMPONENT

Oil-soluble component	Water-soluble component	Water-soluble component concentration (% w/w)									
		0.5		1.0		2.0		4.0		10	
		η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Oleyl alcohol	Cetomacrogol 1000	2	0	2	0	2	0	3	0	6	0
	Sorbester Q12	2	0	2	0	2	0	2	0	4	0
	Cetrimide	2	0	2	0	2	0	4	0	169	1859
	Sodium lauryl sulphate	2	0	3	0	5	0	18	0	48	*
Lauryl alcohol	Cetomacrogol 1000	20	370	16	•	48	440	142	2136	27	352
	Sorbester Q12	17	339	26	577	57	1658	197	2412	284	1758
	Cetrimide	162	2763	×	×	×	×	×	×	×	×
	Sodium lauryl sulphate	58	704	71	999	83	1162	167	1557	140	741
Cetostearyl alcohol	Cetomacrogol 1000	50	1319	102	3019	162	3731	261	4699	55	327
	Sorbester Q12	34	942	165	1187	220	1922	152	1093	29	936
	Cetrimide	118	1922	144	2355	177	2462	72	1721	44	377
	Sodium lauryl sulphate	107	1972	167	2915	175	2588	60	1212	30	150

* Pseudoplastic.
× Traces very irregular.

and 1.0% w/w. His emulsions had a lower phase weight ratio than ours and were subjected to mixing and heating processes after homogenization.

Caution is needed in directly comparing emulsion and gel data, since the exact amount of cetostearyl alcohol transferred to the aqueous phase is not known. However, it may be noted that gels formed by the dispersion of 10% w/w alcohol in varying concentrations of surfactant showed a maximum value of static yield value and apparent viscosity (Table 4). The precise position of the maxima for the latter cannot be

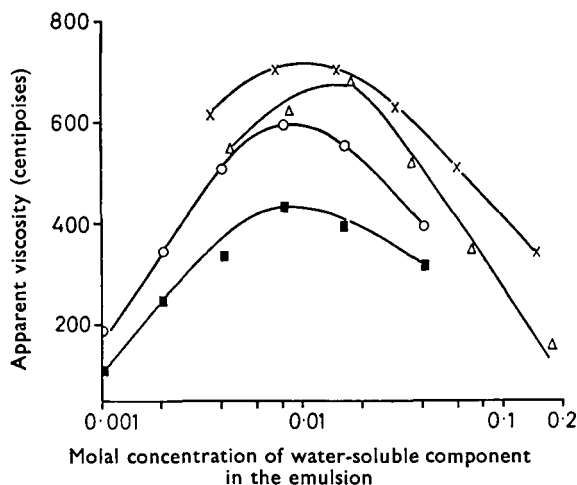


FIG. 3. Effect of water-soluble component concentration (molal) on apparent viscosity of emulsions containing 7% w/w cetostearyl alcohol. ■ Sorbester Q12. ○ Cetomacrogol 1000. △ Sodium lauryl sulphate. × Cetrимide.

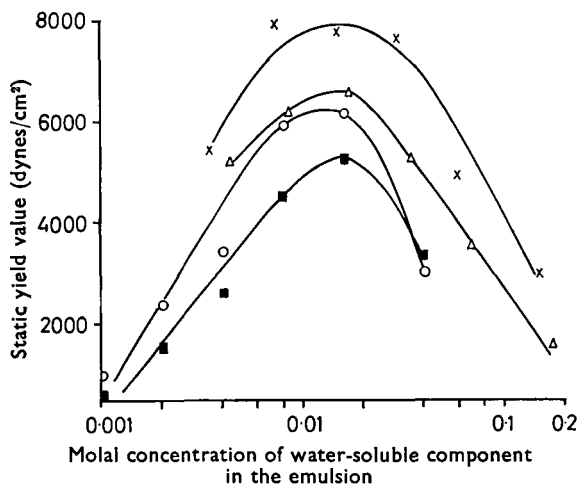


FIG. 4. Effect of water-soluble component concentration (molal) on static yield value of emulsions containing 7% w/w cetostearyl alcohol. ■, Sorbester Q12. ○, Cetomacrogol 1000. △ Sodium lauryl sulphate. × Cetrимide.

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accurately assessed since inspection of the rheograms showed that some samples had not reached an equilibrium value of apparent viscosity at 100 rev/min and 600 sec sweep time.

The gels formed in the external phase of an emulsion by the interaction of cetostearyl alcohol and water-soluble component undoubtedly contain "structure" elements similar in function, but not necessarily in physical form, to those described by Barry & Shotton (1967) who examined aqueous gel systems containing only cetyl alcohol and sodium lauryl sulphate. The composition, number and relative proportion of such elements would presumably alter with the concentration of surfactant. At higher concentrations the amount of cetostearyl alcohol available for the production of "structure" elements may be reduced by solubilization and by complex formation similar to that described by Epstein, Wilson & others (1954).

The values for rheological parameters were generally higher for emulsions prepared with oleyl or lauryl alcohol and an ionic surfactant than with non-ionics. This effect was also apparent with cetostearyl alcohol. The lateral separation of the maxima with respect to percentage composition (Figs 1 and 2) largely disappeared with molal plots (Figs 3 and 4). The percentage concentrations at which the maxima occurred

TABLE 5. EFFECT OF CONCENTRATION OF SOLUMIN FX170SD AND TEXOFOR FX170 ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING OLEYL, LAURYL OR CETOSTEARYL ALCOHOL

Water-soluble component		Oleyl alcohol concentration (% w/w)											
		1		2		4		6		8		10	
	% w/w	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Solumin FX170SD	0.5	11	0	14	0	17	0	19	0	26	0	35	0
	1.0	13	0	14	0	17	0	23	0	29	0	37	0
	2.0	13	0	18	0	31	0	30	0	37	*	49	*
	5.0	34	*	37	*	47	*	59	*	66	*	86	*
Texofor FX170	0.5	16	0	17	0	20	0	25	0	30	0	34	0
	1.0	14	0	16	0	19	0	25	0	32	0	37	0
	2.0	9	0	12	0	19	0	26	0	32	*	41	*
	5.0	34	*	38	*	47	*	53	*	68	*	81	*
		Lauryl alcohol concentration (% w/w)											
Solumin FX170SD	0.5	13	0	14	0	17	0	20	0	29	0	42	0
	1.0	14	0	16	0	17	0	22	0	29	0	40	*
	2.0	21	0	22	0	27	0	28	0	33	0	43	*
	5.0	33	*	38	*	42	*	54	*	70	*	82	*
Texofor FX170	0.5	16	0	13	0	10	0	14	0	16	0	30	0
	1.0	16	0	17	0	20	0	26	0	31	0	36	0
	2.0	10	0	11	0	23	0	27	0	34	*	42	*
	5.0	34	*	38	*	44	*	48	*	61	*	69	*
		Cetostearyl alcohol concentration (% w/w)											
		0.25		0.75		1.5		2.5		4.0		7.0	
Solumin FX170SD	0.5	11	0	13	0	-	-	-	-	-	-	-	-
	1.0	14	0	17	0	69	*	-	-	-	-	-	-
	2.0	27	0	22	0	25	*	-	-	-	-	-	-
	5.0	23	*	33	*	40	*	48	*	361	*	300	2362
Texofor FX170	0.5	13	0	14	0	16	0	49	389	-	-	-	-
	1.0	15	0	15	0	20	0	29	176	-	-	-	-
	2.0	15	0	17	0	22	*	29	101	147	†1156	229	1508
	5.0	31	*	37	*	37	*	45	251	122	603	172	1432

• Pseudoplastic.

† Mean static yield value.

- Emulsions contained wax-like particles and traces were very irregular.

TABLE 6. EFFECT OF WATER-SOLUBLE COMPONENT CONCENTRATION ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF GELS CONTAINING 10% W/W OIL-SOLUBLE COMPONENT

Oil-soluble component	Water-soluble component	Water-soluble component concentration (% w/w)							
		1		2		4		10	
		η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Oleyl alcohol	Solumin FX170SD	1	0	1	0	2	0	4	0
	Texofor FX170	2	0	2	0	3	0	4	0
Lauryl alcohol ..	Solumin FX170SD	1	0	1	0	2	0	4	0
	Texofor FX170	2	0	3	0	4	0	32	*
Cetostearyl alcohol ..	Solumin FX170SD Texofor FX170	←————— Physical dispersions —————→							

* Pseudoplastic.

would therefore appear to be dependent on molecular weight. In a preliminary attempt to elucidate whether the absolute magnitude of the maxima were dependent on molecular weight or charge we have investigated emulsions containing Solumin FX170SD (molecular weight about 1100-anionic), the corresponding non-ionic material Texofor FX170 and Texofor N4, a non-ionic material of low molecular weight (about 300).

The results of these experiments may be seen in Tables 5 and 6. It was found extremely difficult to prepare and test emulsions made with Texofor N4 and all three oil-soluble components, probably due to its solubility (about 2% w/w) in the oil phase. With oleyl and lauryl alcohol, Solumin FX170SD and Texofor FX170 both behaved like the high molecular weight non-ionic surfactants. The emulsions containing low concentrations of cetostearyl alcohol were thin stable fluids but all other members of the series contained wax-like particles which at low concentrations of water-soluble component gave irregular rheograms. Similarly, attempts to form gels produced thin structureless physical dispersions of the alcohol.

The data for emulsions containing Solumin FX170SD and Texofor FX170 with oleyl and lauryl alcohol suggest that molecular weight and probably shape were more important than charge. Results with cetostearyl alcohol yielded no further information in this respect. However, they do support the conclusion, noted previously, that a viscous emulsion will be formed only where the oil-soluble component migrates and interacts to give a gel in the continuous phase.

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