

The rheology of some oil-in-water emulsions stabilized by condensed complex films

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The rheology of emulsions containing oleyl, lauryl or cetostearyl alcohol as the oil-soluble component has been examined. As the concentration of fatty alcohol was increased, three main types of behaviour were found. These could not be explained by the particle size distribution, phase weight ratio or internal phase viscosity. It is suggested that migration of oil-soluble component and subsequent formation of viscous gels in the aqueous phase accounted for the observed behaviour. The effects of temperature, type of oil phase and chemical constitution of water-soluble components, have also been examined.

IN 1940, Schulman & Cockbain showed that oil-in-water emulsions employing a combination of oil- and water-soluble surface-active materials as emulgents, are stabilized by an electrically charged, condensed, intermolecular complex of both components at the interface.

Calculations based on the observed globule size distributions showed that the concentrations of both film-forming components used to produce a series of emulsions containing cetostearyl alcohol were always considerably in excess of those required to form a close-packed monolayer. Since the consistency of these emulsions ranged from thin fluids to semi-solid creams it seemed doubtful whether the interfacial film viscosity played as dominant a role in determining the viscosity of emulsions as was proposed by Schulman & Cockbain (1940). Similar doubts have been expressed by Shotton (1966).

Many factors are known to influence the rheological properties of emulsions; these have been reviewed by Sherman (1964). In particular the control of consistency, by varying the concentration of cetostearyl alcohol in an emulsion, is common pharmaceutical practice. Axon (1956) has shown that increasing concentrations of cetyl alcohol produced increases in both the yield value and plastic viscosity of some emulsions.

The work reported here is part of an investigation of the mechanisms by which cetostearyl and similar alcohols control emulsion rheology, and also the effect of internal phase viscosity, solubility of the fatty alcohol in the disperse phase, chemical constitution of water-soluble component, and other variables.

Experimental

Materials. Polyoxyethylene sorbitan monolaurate (Sorbester Q12) and mono-oleate (Sorbester Q17) (from Howards Ltd., Ilford, Essex), isopropyl myristate, oleyl and lauryl alcohols were commercial grades and were used without further purification. Potassium laurate was prepared by neutralization of the acid. All other materials conformed to the requirements of the B.P. or B.P.C.

Solubility determinations. These were made by the cooling curve method, the results being given in Table 1.

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TABLE I. SOLUBILITY OF CETOSTEARYL ALCOHOL (% W/W) IN VARIOUS OILS

Oils	Temperature, ° C			
	20	25	30	35
Liquid paraffin	0.75	2.0	4.5	14.5
Light liquid paraffin	1.0	2.5	6.25	18.25
Arachis oil	4.0	5.75	8.75	14.0
Castor oil	5.5	9.5	14.0	21.75
Isopropyl myristate	9.0	14.0	23.5	38.5

N.B. The solubility of lauryl and oleyl alcohols is in excess of 30% w/w at 20°. These materials are miscible in all proportions with the oils above 25°.

Preparation of emulsions. Variations in preparation, storage and testing techniques have been shown to affect the properties of emulsions (Cockton & Wynn, 1952; Heinrich & Clements, 1960; Boylan, DeKay & Banker, 1962). A carefully standardized technique has been used to minimize these effects. Except where indicated, the following general formula has been used: liquid paraffin, 50.0 g; oil-soluble component, 0.1 to 10.0 g; water-soluble component, 0.5 g; distilled water to 100.0 g.

Solutions of oil- and water-soluble components, dissolved in the appropriate phases, were mixed at 60°, made up to weight, and homogenized by an Ormerod plate-valve homogenizer, model URF/1 (Ormerod Engineers Ltd., Rochdale, Lancs.). Unless otherwise noted in the text, samples were stored for 24 hr before rheological examination at $25 \pm 0.1^\circ$ in the water bath used to regulate the viscometer plate temperature.

Globule size analysis. A Timbrell Double-Image Micrometer, model A.10 (Fleming Instruments Ltd., Stevenage, Herts.), was used (Barnett & Timbrell, 1962). The emulsions were diluted with 50% v/v aqueous glycerin to give 50 to 100 globules per field, a sample was mounted in a Thoma Haemocytometer Cell, and at least 1000 globules were sized.

A number of globule size distribution functions for emulsions have been proposed (Jellinek, 1950; Schwarz & Bezemer, 1956; Rajagopal, 1959a). Our data showed sufficient conformity to a log-normal distribution for valid comparison of samples to be made without the correction for truncation errors used by Rajagopal (1959b).

Sampling and rheological examination. Flow curves were drawn by a Houston X-Y recorder, model EHR 93-4 (Advance Electronics Ltd., Hainault, Ilford, Essex) coupled, with appropriate gain and impedance matching, to a Ferranti-Shirley cone and plate viscometer (Ferranti Ltd., Moston, Manchester). The latter was fitted with a 3.5 cm radius cone, angle 20.5 mins, and with a 1200 g cm torque spring. The plate temperature was never more than 0.15° below the sample storage temperature, and the effects of draughts were minimized by screening the measuring unit. The cone and plate were equilibrated to the same temperature before use. Silicone fluids, standardized by the method of British Standard 188: 1957, were employed to check the manufacturer's calibration data.

Some change of rheological properties due to sample disturbance is inevitable during transference from the storage container to the viscometer

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plate and during subsequent raising of this plate to the operational position. In an attempt to minimize this effect all samples were drawn into a dip tube and carefully ejected onto the plate. Separate samples were used for each examination.

A sweep-time of 600 sec and a maximum speed of 100 rev/min were used to examine all samples. Under these conditions, where time-dependent flow characteristics were exhibited, an equilibrium value of apparent viscosity was attained at the completion of the up-curve. This value of apparent viscosity (η_{100}) at 100 rev/min (1800 sec⁻¹) has been recorded as one parameter which, irrespective of rheological behaviour, was descriptive of all emulsions.

At low shear rates the up-curves for a number of samples have shown either a spur as described by Levy (1962) or an abrupt change of slope. The shear stress at these points has been reported as the static yield value (SYV). The variation in type of time-dependent behaviour exhibited by our preparations (Fig. 1), often within a closely related series, has precluded the inclusion of values for dynamic yield value and hysteresis loop area.

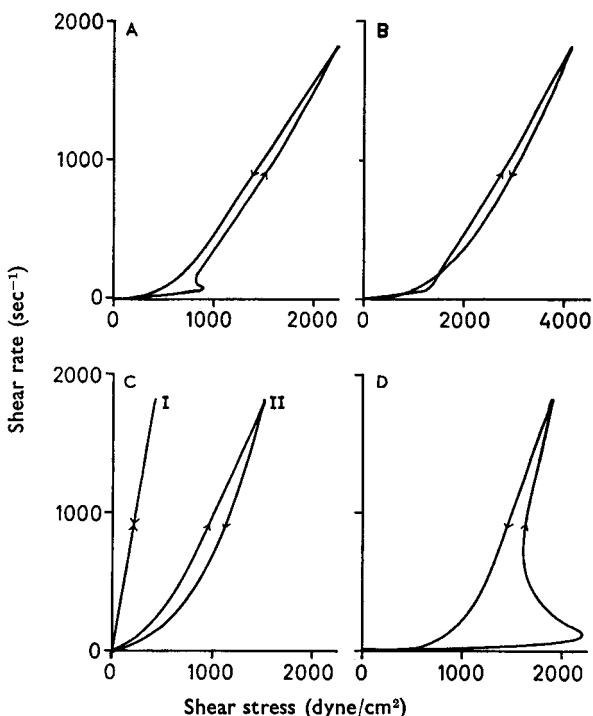


FIG. 1. Rheograms for products of stated composition. A. Cetostearyl alcohol (2.5% w/w)/cetomacrogol 1000 (0.5% w/w). B. Cetostearyl alcohol (4.0% w/w)/sodium lauryl sulphate (0.5% w/w). C. (I) Oleyl alcohol (7.5% w/w)/cetomacrogol 1000 (0.5% w/w), (II) lauryl alcohol (6.0% w/w)/potassium laurate (0.5% w/w). D. Gel containing cetostearyl alcohol (10.0% w/w)/sodium lauryl sulphate (0.5% w/w).

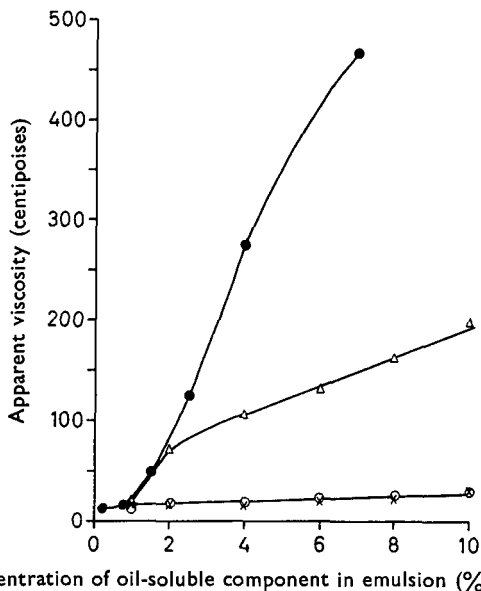


FIG. 2. Effect of oil-soluble component concentration on apparent viscosity in emulsions containing 0.5% w/w water-soluble component. ●, Cetostearyl alcohol/cetomacrogol 1000. △, Lauryl alcohol/sodium lauryl sulphate. ×, Lauryl alcohol/cetomacrogol 1000. ○, Oleyl alcohol/cetomacrogol 1000.

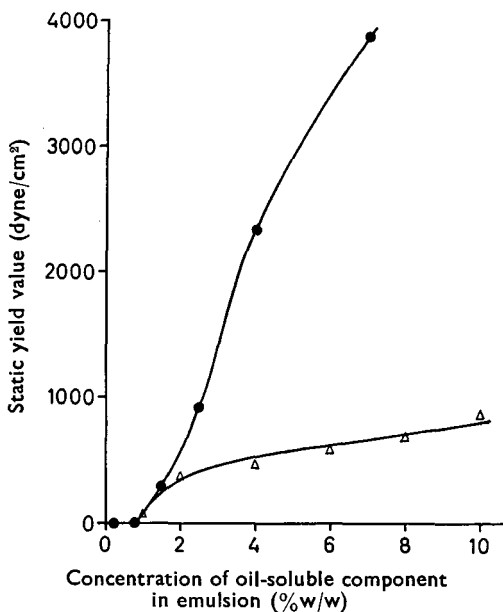


FIG. 3. Effect of oil-soluble component concentration on static yield value in emulsions containing 0.5% w/w water-soluble component. ●, Cetostearyl alcohol/cetomacrogol 1000. △, Lauryl alcohol/sodium lauryl sulphate.

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Results and discussion

Figs 2 and 3 show the three main types of behaviour which were observed when oleyl, cetostearyl or lauryl alcohols were used as the oil-soluble component of emulsions.

All emulsions prepared with oleyl alcohol were fluids of low apparent viscosity (Table 2). Increasing the concentration of this material pro-

TABLE 2. APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING VARYING CONCENTRATIONS OF OLEYL, LAURYL OR CETOSTEARYL ALCOHOL WITH 0.5% W/W WATER-SOLUBLE COMPONENT

Oil-soluble component (% w/w)	Water-soluble component									
	Cetomacrogol 1000		Sorbester Q12		Cetrimide		Sodium lauryl sulphate		Potassium laurate	
	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
Oleyl alcohol										
1.0	11	0	10	0	13	0	15	0	14	0
2.0	16	0	11	0	11	0	11	0	17	0
4.0	18	0	13	0	13	0	15	0	16	0
6.0	21	0	15	0	14	0	19	0	21	0
8.0	25	0	18	0	20	0	23	0	22	0
10.0	27	0	22	0	21	0	30	0	27	0
Lauryl alcohol										
1.0	15	0	15	0	39	151	19	63	13	0
2.0	15	0	15	0	64	352	69	364	17	0
4.0	16	0	19	0	58	477	105	452	25	0
6.0	18	0	20	0	74	503	130	565	85	*
8.0	21	0	23	0	79	691	161	678	165	*
10.0	28	0	25	0	94	754	198	854	210	*
Cetostearyl alcohol										
0.25	12	0	12	0	11	0	14	0	10	0
0.75	15	0	13	0	15	0	18	0	11	0
1.5	51	276	29	126	46	251	53	251	28	151
2.5	126	905	76	1131	130	1005	103	477	42	754
4.0	275	2337	176	1407	269	2412	230	1344	218	2638
7.0	468	3895	336	2638	638	6659	679	6533	†	†

* Pseudoplastic.

† Values too high for measurement with the large cone.

duced only a slight rise in apparent viscosity, which could be attributed to the increase in total disperse phase. Measurable static yield values were not obtained. The water-soluble component used had little effect on the properties of the emulsions.

Low concentrations of cetostearyl alcohol produced fluid emulsions similar to those obtained by the use of oleyl alcohol. As the content of cetostearyl alcohol was raised, a concentration was reached at which the apparent viscosity/concentration curve diverged markedly from that given by emulsions containing oleyl alcohol. Above this divergence concentration static yield values were observed. For emulsions prepared with the water-soluble components given in Table 2, the divergence concentration was identical with the saturation concentration, this latter being the concentration of cetostearyl alcohol in the whole emulsion which was just sufficient to cause saturation of the disperse phase. Slightly higher apparent viscosities and static yield values were found in the case of emulsions containing ionic water-soluble components. At temperatures of 28°, 30° and 35°, or when oils other than liquid paraffin or light

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TABLE 3. EFFECT OF TEMPERATURE ON APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING 50% W/W LIQUID PARAFFIN, 0.5% W/W CETOMACROGOL 1000 AND VARIOUS CONCENTRATIONS OF CETOSTEARYL ALCOHOL

Cetostearyl alcohol (% w/w)	Temperature, ° C									
	20		25		28		30		35	
	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV	η_{100}	SYV
0.25	10	0	10	0	8	0	10	0	13	0
0.50	10	0	11	0	10	0	—	—	11	0
0.75	23	0	17	0	8	0	17	0	12	0
1.0	27	38	19	0	13	0	15	0	11	0
1.25	57	138	33	63	21	38	20	0	—	—
1.5	103	377	61	364	48	176	33	75	—	—
1.75	—	—	74	389	—	—	44	188	—	—
2.0	128	665	87	489	65	402	56	339	28	88
2.5	—	—	130	804	103	628	82	477	—	—
3.0	216	1206	189	1181	—	—	131	867	92	628
4.0	272	1470	243	1432	245	1583	216	1281	143	979
5.0	364	2600	359	2714	347	2671	328	2525	242	1809
5.5	388	2864	374	2814	—	—	349	2814	—	—
6.0	—	—	377	2864	380	2965	—	—	309	2512
7.0	—	—	—	—	—	—	—	—	423	3568
7.5	—	—	565	4208	—	—	478	3769	—	—

TABLE 4. APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF EMULSIONS CONTAINING CETOSTEARYL ALCOHOL AND 0.5% W/W CETOMACROGOL 1000 WITH DIFFERENT OIL PHASES

Liquid paraffin	Cetostearyl alcohol % w/w	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	3.5	—
	η_{100} SYV	14 0	18 0	24 0	29 75	58 276	78 440	105 565	125 704	290 2060	— —
Light liquid paraffin	Cetostearyl alcohol % w/w	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	3.5	—
	η_{100} SYV	14 0	15 0	18 0	21 0	37 88	56 264	71 339	105 628	261 1885	— —
Isopropyl myristate	Cetostearyl alcohol % w/w	4.75	6.0	6.5	6.75	7.0	7.25	7.5	7.75	8.0	9.75
	η_{100} SYV	31 0	60 276	76 415	114 653	131 817	155 1005	183 1281	214 1533	237 1771	395 3317
Arachis oil	Cetostearyl alcohol % w/w	0.25	1.75	2.0	2.75	3.0	3.25	3.75	5.0	7.5	10.0
	η_{100} SYV	10 0	24 0	28 75	60 377	94 533	94 533	143 1030	268 2588	464 4259	591 6433
Castor oil (1) (constant oil concentration)	Cetostearyl alcohol % w/w	2.0	4.0	4.25	4.5	4.75	5.0	5.25	5.5	7.5	10.0
	η_{100} SYV	19 0	85 276	89 377	107 565	129 766	139 879	151 980	166 1156	339 2299	416 3593
Castor oil (2) (constant total disperse phase concentration)	Castor oil % w/w	48.0	47.0	46.0	45.25	44.75	44.0	43.0	—	—	—
	Cetostearyl alcohol % w/w	2.0	3.0	4.0	4.75	5.25	6.0	7.0	—	—	—
	η_{100} SYV	14 0	27 0	57 138	102 616	133 854	198 1206	275 1709	—	—	—

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liquid paraffin were used, the divergence concentration was less than the appropriate saturation concentration (Tables 3 and 4). As cetostearyl alcohol was found to be more soluble in the disperse phase under these conditions, the phase weight ratio increased correspondingly for a series of emulsions which included samples at and above the saturation concentration. The difference between the divergence and saturation concentrations was reduced, but not eliminated, with castor oil emulsions of constant phase weight ratio.

At 25°, lauryl alcohol, like oleyl, was miscible in all proportions with liquid paraffin. The rheological behaviour of emulsions containing lauryl alcohol was dependent on the type of water-soluble component. Fluid products of low apparent viscosity were obtained with non-ionic components, but ionic materials produced more viscous emulsions, some of which exhibited static yield values (Table 2). Their apparent viscosities and static yield values were intermediate between those of comparable products based on cetostearyl or oleyl alcohol.

Only minor differences in globule size and size distribution were found for a representative selection of emulsions (Table 5). These differences

TABLE 5. EXAMPLES OF GLOBULE SIZE DISTRIBUTION DATA FOR EMULSIONS CONTAINING 50% W/W LIQUID PARAFFIN, 0.5% W/W WATER-SOLUBLE COMPONENT AND THE STATED CONCENTRATION OF OIL-SOLUBLE COMPONENT

Water-soluble component	Oil-soluble component	Oil-soluble component (% w/w)	Geometric mean diameter (μ)	Standard deviation of mean ln. diameter
Cetomacrogol 1000	cetostearyl alcohol	0.25	1.93	0.477
Cetomacrogol 1000	cetostearyl alcohol	1.5	1.80	0.396
Cetomacrogol 1000	cetostearyl alcohol	4.0	1.75	0.387
Sorbester Q12 ..	oleyl alcohol	2.0	2.15	0.502
Sorbester Q12 ..	oleyl alcohol	6.0	2.08	0.493
Sorbester Q12 ..	oleyl alcohol	10.0	2.25	0.525
Sodium lauryl sulphate ..	oleyl alcohol	2.0	1.88	0.502
Potassium laurate ..	oleyl alcohol	2.0	1.80	0.544
Sorbester Q12 ..	lauryl alcohol	2.0	1.80	0.477
Cetrimide ..	cetostearyl alcohol	4.0	1.53	0.454

could not account for the observed pattern of results, although they may affect the absolute values of apparent viscosity and static yield value of individual preparations. The qualitatively similar behaviour of emulsions with constant oil and constant total disperse phase concentration led to the conclusion that phase weight ratio effects were not responsible for the rheological behaviour of our emulsions.

A comparison of the data for preparations based on a disperse phase of isopropyl myristate or castor oil (viscosities of 3 and 600 centipoises respectively) showed that internal phase viscosity was not a major factor determining the flow properties of our emulsions. Similar results for concentrated emulsions have been reported by Toms (1941) and by Shotton & White (1960). Nawab & Mason (1958) suggested that emulsion globules may behave like rigid spheres when stabilized by an interfacial film. Under these conditions the flow properties of emulsions would not be much influenced by internal phase viscosity. For this reason we rejected the possibility that increased viscosity of oil globules,

due to precipitation of excess cetostearyl alcohol, was responsible for the pronounced change in rheological properties above the divergence concentration. We have also failed to observe the lattice arrangement of particles characteristic of such systems during microscopical examination of our emulsions.

Time-dependent rheological properties are known to be associated with structure formation in the dispersing medium (Woodman & Marsden, 1966); such properties were a feature of a number of our emulsions. This, coupled with the apparent absence of cetostearyl alcohol from the internal phase, prompted us to investigate the possible modification of external phase viscosity. Many authors (Matalon, Salton & Cohen, 1951; Epstein, Wilson & others, 1954; Becher & Del Vecchio, 1964) have reported complex formation between fatty alcohols and surface-active agents in aqueous solution. We found viscous gels were formed by the interaction of cetostearyl alcohol, and in some instances lauryl alcohol, with solutions of the water-soluble components used in these studies. Oleyl alcohol did not form gels under these conditions. The viscosity of the aerosol emulsions examined by Sanders (1966) may be attributed to the use of preformed viscous gels of this type. The rheograms of the gels we have investigated exhibited hysteresis loops; their apparent viscosities and static yield values are given in Table 6. Generally, the flow data for the gels reflected the behaviour of corresponding emulsions.

TABLE 6. APPARENT VISCOSITIES (η_{100} IN CENTIPOISES) AND STATIC YIELD VALUES (SYV IN DYNES/CM²) OF GELS CONTAINING 10% W/W CETOSTEARYL OR LAURYL ALCOHOLS AND 0.5% W/W WATER-SOLUBLE COMPONENT

Water-soluble component	Cetostearyl alcohol		Lauryl alcohol	
	η_{100}	SYV	η_{100}	SYV
Cetomacrogol 1000	50	1319	20	370
Sorbester Q12	34	942	17	339
Cetrimide	118	1922	162	2763
Sodium lauryl sulphate	107	1972	58	704
Potassium laurate	129	2525	187	3995

The formation of gels would necessitate the migration of fatty alcohol from the oil to the aqueous phase. Migration of sorbitan monolaurate between emulsion phases has been reported by Sherman (1963). During homogenization the intense agitation and enormous extension of the interface provide the most favourable conditions for transfer of oil-soluble component, although this could continue during storage. Apparently, the process was virtually completed within 24 hr, as prolonged storage caused only insignificant changes in the flow properties of our emulsions.

Since lauryl alcohol was completely miscible with liquid paraffin at 25°, the equilibrium concentration of the alcohol in both phases was probably governed by those factors affecting a typical partitioning process. A more complicated transfer mechanism may be involved where emulsions contained cetostearyl alcohol in excess of its solubility in the disperse

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phase. The close similarity of the divergence and saturation concentrations for some emulsions suggests that equilibrium was attained when such excess cetostearyl alcohol had been transferred to the aqueous phase. In those cases where the divergence concentration was less than the saturation concentration, it would appear that migration of cetostearyl alcohol continued below the saturation concentration, perhaps by a partitioning process similar to that proposed for lauryl alcohol.

Although many physico-chemical factors undoubtedly influence the migration process, the extent to which this occurs, and the "intrinsic" strength of the gel so formed, appear to be major factors determining the rheological properties of emulsions stabilized by a condensed complex interfacial film.

Acknowledgements. We thank the Pharmaceutical Society of Great Britain for an educational grant to one of us (E.M.R.) and for a grant to purchase the Timbrell Double-Image Micrometer. Our thanks are also due to Dr. R. E. Stuckey, The British Drug Houses Ltd., for many helpful discussions during the course of this work.

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