

WATER-SOLUBLE CELLULOSE DERIVATIVES*

USES AS PRIMARY EMULSIFYING AGENTS. PART I

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The ability of methyl-, methylethyl-, and sodium carboxymethyl-cellulose to promote emulsions with liquid paraffin and arachis oil is largely independent of the viscosity of their mucilages. Methyl- and methylethyl-cellulose are more efficient emulsifying agents than is sodium carboxymethylcellulose. Emulsifying efficiency increases with the concentration of the derivative, and low viscosity grades are more efficient than high viscosity grades. Mixtures of these derivatives have little advantage as emulsifying agents over methyl- and methylethyl-cellulose used singly.

EARLIER work^{1,2} was concerned with determining the factors influencing the viscosity of aqueous dispersions of certain water-soluble cellulose derivatives. The purpose of this investigation was to study the use of these same derivatives as emulsifying agents, and, in the light of our previous findings, to attempt to clarify the role of viscosity and other factors in emulsion formation and stability. The effects of varying the concentration, viscosity grade and type of derivative are discussed.

MATERIALS

The cellulose derivatives used included six viscosity grades of methyl-cellulose,† one viscosity grade of methylethylcellulose,‡ and three viscosity grades of sodium carboxymethylcellulose.§ The substances emulsified were liquid paraffin B.P. and arachis oil B.P. Chemicals were of A.R. quality.

METHODS

Our previous work showed that the usual accelerated storage tests would be unsuitable for emulsions made with the cellulose derivatives. In the experiments described below, emulsions were stored for periods of up to 1 year, during which globule counts and macroscopic examinations were made at frequent intervals.

Preparation of Emulsions

Mucilages were prepared as previously described¹ and were allowed to stand for 24 hours. Emulsions (200 ml. quantities) containing 25 per cent v/v of liquid paraffin or arachis oil were made by adding the mucilage to the oil and mixing with a propeller at a speed of 3000 revs./min. for

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† Celacol M20, M50, M100, M450, M2500 (British Celanese Ltd.); Methocel 4000 (Dow Chemical Co.).

‡ Edifas A (Imperial Chemical Industries Ltd.).

§ Cellofas B, low, medium and high (Imperial Chemical Industries Ltd.).

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10 minutes. The product was passed once through a hand-operated homogeniser and left to stand for 24 hours before examination.

Globule Counting

The method of globule counting was based on the techniques described by Cockton and Wynn³ and Levius and Drommond⁴, using a haemocytometer of 1/10 mm. depth and a ruled disc in the microscope eyepiece. Results were expressed as the value of "H", which is the number of millions of globules into which 1 cu. mm. of oil has been subdivided.

Reproducibility of Results

Some emulsions, particularly those which were later found to be the least stable, broke on dilution. The most stable emulsion appeared to be that containing a high concentration (3.375 per cent w/v) of a low viscosity grade (Celacol M20) of methylcellulose. Counts on 40 samples of a single batch of this emulsion gave a coefficient of variation of 10.75 per cent, and on single samples of 20 different batches 10.25 per cent. This indicated that the variation resided in the sampling, diluting and counting, rather than in the preparation of the emulsions. We attribute it largely to a small but variable degree of break-down on dilution.

The following procedure was adopted. Emulsions were prepared in duplicate and three counts were made on each batch. If the coefficient of variation of the six counts was less than 10 per cent, the mean was recorded; if not, the emulsions were examined macroscopically only. Subsequently, one sample of each batch was counted. If the variation was within the above limits the mean was recorded; if not, a further three samples of each batch were examined before discontinuing the counts and relying solely on macroscopic observations.

EXPERIMENTAL AND RESULTS

(I) CELLULOSE ETHERS USED SINGLY

Liquid paraffin emulsions. Emulsions of liquid paraffin made with methyl-, methylethyl-, and sodium carboxymethyl-cellulose were stored for 1 year at room temperature and examined at 1 day, 1, 2, 4, 8, 12, 24, 36 and 52 weeks. The results (Tables I to III) show that: (a) The higher the concentration of emulsifying agent, the larger was the "H" value and the greater the stability of the emulsion. (b) The lower the viscosity grade of the emulsifying agent, the higher was the "H" value and the greater the stability of the emulsion. This is so whether the emulsions are compared for concentration or the viscosity of the continuous phase. (c) Methylethylcellulose yielded coarser emulsions than the low viscosity grades of methyl- and sodium carboxymethyl-cellulose. They were, however, more stable than methylcellulose emulsions, and sodium carboxymethylcellulose emulsions were the least stable.

Arachis oil emulsions. Emulsions of arachis oil made with methylcellulose, and the low viscosity grades of methyl- and sodium carboxymethyl-cellulose were stored for 6 months at room temperature and

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TABLE I*

SHELF STORAGE OF LIQUID PARAFFIN EMULSIONS MADE WITH METHYLCELLULOSE

Derivative grade	Concentration (per cent)	Efflux time of mucilage (sec.)	Value of "H"		Coefficient of variation	Cream volume (per cent)	Stage of oil separation (weeks)	Remarks
			Initial	Final				
M20	4.5	540	46.3	48.1 (52)	7.5	50 (24, 52)	—	Thick, pourable
	4.0	345	46.9	48.2 (36)	10.9	50 (24, 52)	—	Thick, pourable
	3.0	145	35.2	33.3 (36)	9.6	50 (24) 25 (52)	36-52	Fluid
	2.0	63	18.4	19.5 (24)	6.8	33 (1) 25 (52)	24-36	Very fluid
	1.0	38	13.9	16.0 (1)	—	33 (1) 25 (52)	1-2	Very fluid
M50	2.5	510	9.3	8.9 (12)	8	75 (1, 52)	12-24	Thick, pourable
	2.0	246	9.1	6.9 (4)	11	50 (1) 33 (52)	8-12	Thick, pourable
	1.5	122	6.0	7.3 (1)	—	50 (1) 33 (24, 52)	8-12	Fluid
	1.0	59	—	—	—	50 (1) 25 (52)	2-4	Very fluid
	0.5	39	—	—	—	50 (1) 25 (52)	0	Incompletely emulsified
M100	2.25	648	5.5	4.9 (2)	14.5	66 (4, 52)	8-12	Thick, pourable
	2.0	417	5.7	5.1 (4)	11	50 (12, 52)	8-12	Thick, pourable
	1.5	180	6.8	—	—	33 (2, 52)	8-12	Fluid
	1.0	75	—	—	—	33 (2, 52)	1-2	Very fluid
	0.5	41	—	—	—	33 (2, 52)	0	Incompletely emulsified
M450	1.5	422	Not examined					Good appearance but broke down on dilution
M2500	1.0	450	Not examined					Incompletely emulsified
4000	0.9	450	Not examined					Incompletely emulsified

*EXPLANATORY NOTES

TABLES I TO V

Concentrations. These refer to the percentage w/v of derivative in the mucilage used to prepare the emulsions. (Emulsions contain 25 per cent v/v of oil.)

Final value of "H." Figures in parenthesis indicate stage, in weeks, of last globule count.

Coefficient of variation. Calculated on all globule counts made during the period of storage (see also previous note).

Cream volume. Figures in parenthesis indicate stage, in weeks, of observation. The volumes were assessed by means of a rule placed against the sides of the jars.

Oil separation. Unless otherwise stated, this refers to the separation of small isolated globules, visible to the naked eye, on the surface of the emulsion.

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TABLE II

SHELF STORAGE OF LIQUID PARAFFIN EMULSIONS MADE WITH METHYLETHYLCELLULOSE

Concentration (per cent)	Efflux time of mucilage (sec.)	Value of "H"*	Cream volume (per cent)	Stage of oil separation (weeks)	Remarks
4.0	449	—	75 (24) 50 (52)	—	Thick, pourable
3.5	240	—	75 (8) 50 (52)	—	Thick, pourable
3.0	138	20.6 20.8 (4 weeks)	75 (1) 50 (12,52)	—	Readily pourable
2.0	60	15.5	50 (1, 52)	36-52	Fluid
1.0	36	10.7	50 (1, 52)	36-52	Very fluid

* In many instances clumping of globules around the partially-etherified fibre particles in the thick emulsions and in the cream layers of the less viscous samples made it impossible to prepare adequately dispersed dilutions for counting purposes. Unless otherwise stated, the value quoted is the initial "H" value.

examined at 1 day, 1, 2, 4, 8, 12, and 24 weeks. The results (Table IV) show that (a) Although methyl- and methylethyl-cellulose promoted emulsions which had higher "H" values than the corresponding liquid paraffin emulsions, they were generally much less stable. Methylethyl-cellulose appeared to be the better emulsifying agent for arachis oil. (b) Generally, the higher the concentration of emulsifying agent, the greater was the stability of the emulsion. (c) Sodium carboxymethyl-cellulose failed to completely emulsify the arachis oil.

(II) CELLULOSE ETHERS USED IN COMBINATION

Emulsions of liquid paraffin and arachis oil made with various mixtures of the ethers were stored for 6 months at room temperature and examined at 1 day, 3 months and 6 months. Comparison of the results, summarised in Table V, with those set out in the earlier tables leads to the following general observations.

Liquid paraffin emulsions. The combination of methylcellulose M20 with higher viscosity grade derivatives made for far greater emulsifying efficiency than would have been achieved by the latter components alone in the concentrations used in the mixture. If mucilages of approximately equal viscosities are considered, methylcellulose M20 used alone promoted more stable emulsions than did any combination of it with the other derivatives. Similarly, if the basis of comparison is mucilages of equal concentration the mixed emulsifying agents do not offer any advantage over methylcellulose M20 used alone.

Methylethylcellulose mixtures gave similar results, except that those containing low or medium grades of sodium carboxymethylcellulose as the other component gave more stable emulsions than did 1 per cent methylethylcellulose alone.

Arachis oil emulsions. Although all the emulsions made with the methylcellulose mixtures showed oil separation after 12 weeks' storage, they were more efficient emulsifying agents for arachis oil than any of the components used singly.

TABLE III
SHELF STORAGE OF LIQUID PARAFFIN EMULSIONS MADE WITH SODIUM
CARBOXYMETHYLCELLULOSE

Derivative grade	Concentration (per cent)	Efflux time of mucilage (sec.)	Value of "H"		Coefficient of variation	Cream volume (per cent)	Stage of oil separation (weeks)	Remarks*
			Initial	Final				
Low	3.675	573	47.8	53.3 (24)	9	75 (36) 50 (52)	12-24	Thick, pourable
	3.25	387	54.2	52.4 (2)	2.2	75 (36) 50 (52)	12-24	Thick, pourable
	2.5	160	—	—	—	50 (24) 33 (52)	4-8	Pourable. Incompletely emulsified before homogenisation
	1.5	64	—	—	—	—	0	Incompletely emulsified
	1.0	42	—	—	—	—	0	Incompletely emulsified
Medium	1.3	575	40.5	41.8 (4)	1.7	0	4-8	Thick, pourable. Incompletely emulsified before homogenisation
	1.1	340	31.9	31.8 (1)	—	95 (8) 75 (24, 52)	2-4	As above
	0.9	182	—	—	—	—	0	Incompletely emulsified
	0.7	103	—	—	—	—	0	As above
	0.5	63	—	—	—	—	0	As above
High	1.0	536	18.9	18.4 (1)	—	0	2-4	Incompletely emulsified before homogenisation. Pools of oil had separated by 24 weeks
	0.9	349	18.4	—	—	50 (2) 25 (24, 52)	1-2	As above
	0.7	207	—	—	—	—	0	Incompletely emulsified
	0.5	101	—	—	—	—	0	As above
	0.3	51	—	—	—	—	0	As above

* There was no difference in the behaviour of emulsions stored in the light and in the dark.

The mixtures containing methylethylcellulose were more efficient emulsifying agents than any of the components alone in the concentrations used in the mixture. However, they were generally no more efficient than methylethylcellulose used alone in equivalent concentration, and much less efficient than this derivative used in concentrations yielding mucilages of equivalent viscosity.

DISCUSSION

Influence of Viscosity Grade

Because the cellulose derivatives have the common property of yielding viscous dispersions in water, they have been regarded as emulsion-stabilisers rather than emulsion-promoters. Our results show, however,

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TABLE IV

SHELF STORAGE OF ARACHIS OIL EMULSIONS

Derivative	Concentration (per cent)	Efflux time of mucilage (sec.)	Value of "H"*	Cream volume (per cent)	Stage of oil separation (weeks)	Remarks
Methyl M20	4.5	546	141.6 147.6 (8 weeks)	0	—	Thick, pourable. The surface became oily and granular by 24 weeks
	3.0	149	136	0	—	As above
	2.0	61	—	25 (24)	12-24	Frank breakdown on storage
	1.0	37	—	25 (24)	12-24	As above
Methyl-ethyl	4.0	452	231.6	0	—	Thick, pourable. Counts discontinued because of dispersion difficulties
	3.0	145	176	75 (24)	12-24	As above
	2.0	60	—	50 (24)	12	Fluid. Granular appearance and thin continuous oil film by 24 weeks
	1.0	35	—	50 (12, 24)	12	Very fluid. "Pitted" surface with free oil by 24 weeks
S.C.M.C. (low)	3.675 and under	570 and under	—	—	0	All incompletely emulsified

* Unless otherwise stated the value quoted is the initial "H" value.

that some of them are efficient primary emulsifying agents and, further, that their ability to promote emulsions owes little to the viscosity, as such, of their mucilages.

One of the most interesting aspects of this work was the higher emulsifying efficiency of low as compared with high viscosity grade derivatives. This was particularly well marked in the methylcellulose series. The explanation may lie in the rates at which the various derivatives diffuse to the interface. It is known that some low molecular weight agents diffuse more rapidly to the interface than high molecular weight agents of analogous structure, although the latter may ultimately be more strongly adsorbed⁵. It is for this reason sometimes considered advantageous to use a mixture of low and high molecular weight agents as an emulgent.

Influence of Concentration

An increase in the concentration of emulsifying agent led to a decrease in the size of the dispersed particle. At the same time, irrespective of the viscosity of the continuous phase, the "H" values of any group of emulsions increased as the viscosity grade of the emulsifying agent decreased, and there were also differences in the "H" values obtained with the various derivatives. Also, mucilages which had been appreciably

TABLE V

SHELF STORAGE OF LIQUID PARAFFIN AND ARACHIS OIL EMULSIONS MADE WITH MIXTURES OF DERIVATIVES

Derivatives	Efflux time of mucilage (sec.)	Disperse phase*	Value of "H"†	Cream volume (per cent)	Stage of oil separation (weeks)	Remarks
Methyl M20 1 per cent and S.C.M.C. (low) 2.5 per cent	633	A	23.5	50 (24)	24	Thick, pourable. Oil film on surface by 24 weeks
		B	252.0	0	12	Thick, pourable. Frank break-down by 12 weeks
Methyl M20 1 per cent and S.C.M.C. (medium) 0.8 per cent	567	A	—	80 (12) 50 (24)	24	Thick, pourable. Oil film by 24 weeks
		B	249.2	0	12	Thick, pourable. Frank break-down by 12 weeks
Methyl M20 1 per cent and S.C.M.C. (high) 0.6 per cent	632	A	—	75 (24)	24	Thick, pourable
		B	194.2	0	12	Thick, pourable. Frank break-down by 12 weeks
Methyl M20 1 per cent and Methyl 4000 0.65 per cent	520	A	—	40 (12, 24)	12	Thick, pourable
		B	58.8	0	12	Thick, pourable. Frank break-down by 12 weeks
Methylethyl 1 per cent and S.C.M.C. (low) 2.5 per cent	646	A	26.2	75 (24)	—	Thick, pourable
		B	182.4	0	12	Thick, pourable
Methylethyl 1 per cent and S.C.M.C. (medium) 0.8 per cent	530	A	16.4 15.3 (12 weeks)	75 (12) 60 (24)	—	Thick, pourable
		B	47.2	25 (24)	12	Thick, pourable
Methylethyl 1 per cent and S.C.M.C. (high) 0.6 per cent	680	A	4.3	75 (12) 60 (24)	12	Thick, pourable
		B	72.0	25 (24)	12	Thick, pourable
Methylethyl 1 per cent and Methyl 4000 0.65 per cent	502	A	—	75 (12) 50 (24)	12	Thick, pourable Very coarse
		B	39.8	50 (24)	12	Thick, pourable. Granular appearance by 24 weeks

* A = liquid paraffin, B = arachis oil.

† Unless otherwise stated the value quoted is the initial "H" value.

reduced in viscosity by heating yielded emulsions which had "H" values similar to others made with the undegraded mucilages⁶. The degree of dispersion, therefore, must be chiefly determined by some factor other than viscosity but which varies with the concentration of the emulsifying agent. Interfacial tension experiments suggest that this factor is the rate and extent of adsorption of the emulsifying agent at the interface^{7,8}.

Fordham⁷ found that the interfacial tension between a solution of

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sodium carboxymethylcellulose and liquid paraffin decreased as the strength of the solution increased until a concentration of between 0.88 and 1.4 per cent was reached. For still stronger solutions the interfacial tension was independent of concentration. With methylethylcellulose solutions interfacial tension remained independent of concentration when a strength of 0.38 per cent was reached. Although the range of concentrations over which interfacial tension decreases is narrower than that over which we have observed variations in "H" values, Fordham's records of interfacial tension as a function of time showed that the initial rate of fall was greatest for the strongest solutions. This would explain why we continued to obtain progressively higher "H" values as the concentration of emulsifying agent was increased to relatively high levels.

Influence of Derivative

Methyl- and methylethyl-cellulose were much more efficient emulsifying agents for both liquid paraffin and arachis oil than was sodium carboxymethylcellulose. Since the sample of methylethylcellulose contained a proportion of only partially-etherified fibre¹ it is difficult to compare its efficiency with that of methylcellulose on a concentration basis. Aesthetically, methylethylcellulose emulsions were unsatisfactory. Not only did the derivative produce more foam than methylcellulose, but, on storage, the partially-etherified fibre separated to give a third and sometimes even a fourth layer in creaming emulsions. Nevertheless, it emulsified very readily and emulsions containing it in adequate concentration were extremely stable. For arachis oil it was the best emulsifying agent, and it is possible that a "purer" sample would have proved generally superior to methylcellulose. Morrison and Campbell⁸ also considered methylethylcellulose a better emulsifying agent than sodium carboxymethylcellulose, particularly at low concentrations, and both they and Fordham⁷ have related their observations to the results of interfacial tension studies. Morrison and Campbell preferred a high rather than a low grade of sodium carboxymethylcellulose for emulsifying liquid paraffin, but they found that when the concentration was reduced to 1 per cent or less emulsification became progressively more difficult. Our results show that higher concentrations of lower viscosity grades are far more efficient as emulsifying agents than lower concentrations of higher viscosity grades. Like us, Morrison and Campbell found that the presence of methylethylcellulose improved the emulsifying ability of sodium carboxymethylcellulose, but apart from the fact that such mixtures foamed less we are not convinced that they offer any special advantage over methylethylcellulose used alone. Sodium carboxymethylcellulose itself is unsatisfactory as an emulsifying agent for arachis oil; indeed, it would seem that liquid paraffin is one of the few substances with which it can be used with any degree of success⁸.

Degree of Dispersion and Stability

The stability of an emulsion is not necessarily a function of its degree of dispersion. An emulsion promoted by a mucilage which had been

reduced in viscosity by heating deteriorated very much more rapidly than one made with the unheated mucilage, although both, initially, had similar "H" values⁶. Again, arachis oil emulsions had considerably higher "H" values initially than did liquid paraffin emulsions, yet the former were much less stable than the latter. And although in the liquid paraffin series, some of the sodium carboxymethylcellulose emulsions yielded the highest "H" values recorded, and the methylethylcellulose emulsions the lowest, the former were generally the most unstable and the latter the most stable of the series.

Observations on the Globule Counting Procedure

Because of the tendency of the emulsions to break down on dilution, the method as applied has not proved a generally suitable one for long-term stability studies on cellulose derivative emulsions. Only with a few emulsions was it possible to continue the counts over the entire storage period, and, since these were in fact the most stable emulsions, the globule counts remained largely unaltered. Those emulsions which subsequently proved to be unstable broke on dilution before the incipient instability could be demonstrated. In no instance, therefore, has it been possible to detect any deterioration by microscopical examination. These difficulties apart, the quantitative results have provided some support for the conclusions drawn from the macroscopic observations, and the initial counts, in particular, have shed an interesting light on the comparative emulsifying properties of the various derivatives studied.

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