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Effect of Alcohol Content on Emulsion Stability of Cream Liqueurs

William Banks & D. Donald Muir

The Hannah Research Institute, Ayr, Scotland, Great Britain

ABSTRACT

Factors controlling the emulsion stability of cream liqueurs with high alcohol contents have been studied. It is shown that, as the alcohol content of the cream liqueur increases, the emulsion becomes increasingly sensitive to the interaction between compositional parameters and processing conditions. In addition, it was found that the alcohol content of the liquid phase, rather than the total alcohol content, determines stability.

INTRODUCTION

A substantial market has been developed in the last decade for cream liqueurs. Trade in these products, based on cream, sodium caseinate, sugar and various spirits, amounts to at least 17 million litres per annum from the British Isles alone and is equivalent to over 2500 tonnes of butterfat. A large proportion of the total production is exported to the USA, Canada and Australia. The principle of preparation of stable emulsions for use in cream liqueurs has been detailed (Banks *et al.*, 1981*a*) and it has been shown that long-term stability of product is highly dependent on the efficient control of calcium-induced aggregation (Banks *et al.*, 1981*b*, 1982, 1983). Provided the principles described by Banks *et al.* (1983) are followed, cream liqueur may be reliably manufactured from

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a wide range of spirit bases. However, some potential export markets (e.g. the Republic of South Africa) have imposed restrictions on the composition of imported cream liqueurs. For example, it is specified that imported liqueurs contain 24% (v/v) ethanol, rather than 17% (v/v) ethanol, if the liqueur is produced within that country. It is not feasible to manufacture cream liqueurs with 24% (v/v) ethanol using conventional methodology. This paper reports on investigations of factors controlling the stability of cream-based emulsions at high alcohol levels with a view to increasing emulsion stability.

MATERIALS AND METHODS

Model cream liqueurs were prepared by the method shown schematically in Fig. 1. The homogenised intermediate was prepared as described by Banks *et al.* (1982), cooled to 10 °C and neutral spirit (96% vol, 168° proof) was added. Products made in this way showed little immediate evidence of emulsion destabilisation. In later experiments, cream liqueurs were manufactured using washed cream and all the alcohol was added before homogenisation. Washed cream was prepared as shown in Fig. 2. Water (8 volumes) was added to double cream (3 volumes), mixed

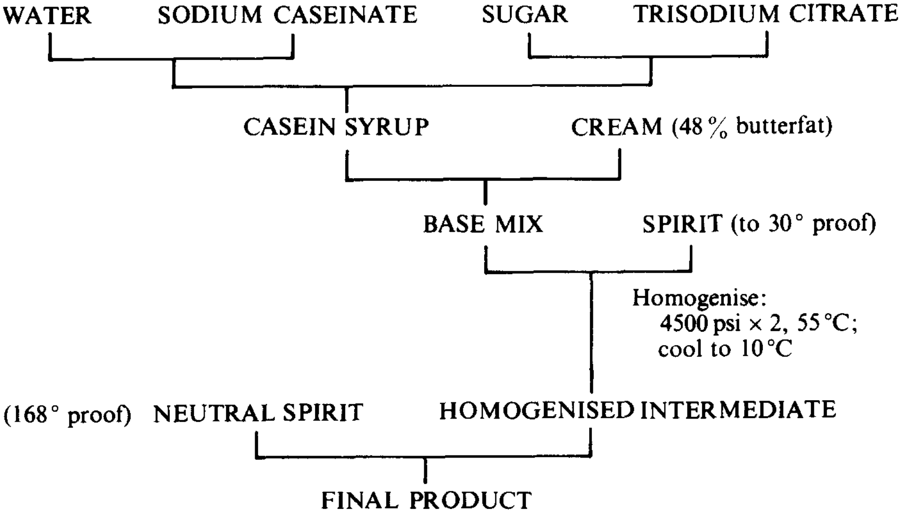

Fig. 1. Schematic diagram for preparation of high-proof emulsions.

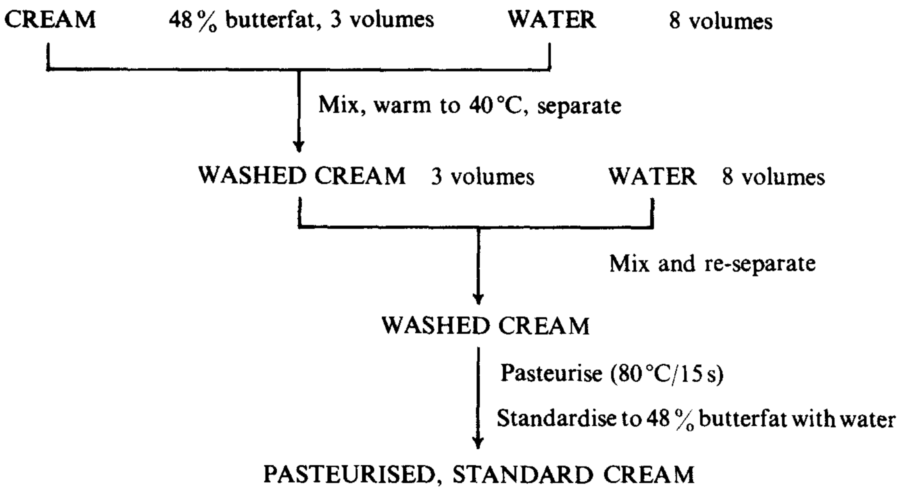

Fig. 2. Preparation of washed cream.

thoroughly then re-separated at 40 °C. The resulting cream was then re-suspended in warm water and further separated. The cream was standardised to 48 % butterfat with water and pasteurised. The product was cooled and stored at 5 °C until required.

The fat, crude protein, sugar and total solids contents of the liqueurs were estimated by the methods of Banks *et al.* (1981*b*).

Viscosity was measured using a rotational viscometer (Model LVTD, Brookfield Engineering Labs Inc., Stoughton, USA) fitted with a temperature-controlled small sample holder. All measurements were made at a final shear rate of $79\,s^{-1}$.

The weight fraction of fat globules exceeding 0·5 and 1·0 μm in diameter was measured using a Coulter Counter (Model ZM, Coulter Electronics) and a 20 μm orifice. Before estimation of globule size, the emulsions were diluted 1:10 000 with Isoton II (Coulter Electronics).

The stability of the product was taken as the time that elapsed at 45 °C before visible separation of the emulsion was observed.

RESULTS AND DISCUSSION

The modified manufacturing process

The immediate aim of this work was to develop a method of manufacturing cream liqueurs of high alcohol content, i.e. 40° proof and above. Our standard technique (Banks *et al.*, 1982), in which sodium caseinate is dissolved in water and sugar, cream, alcohol and stabiliser (trisodium citrate) are added and the mixture homogenised (2 × 4500 psi, at 55 °C), yielded a product deficient in shelf-life. Accelerated storage testing, carried out at 45 °C, resulted in the rapid onset of two limiting phenomena—gelation, with consequent serum separation, and creaming. The former defect is observed in all cream liqueurs after prolonged storage at 45 °C, but the latter has not been seen previously. The creaming phenomenon is quite distinct from the formation of fat plugs, which is due merely to inadequate homogenisation. Rather, creaming appeared to be an aggregation process, similar in some respects to the phenomenon of gelation. When liqueur containing 42° proof alcohol and 40% total solids was prepared, overnight storage of the product at 45 °C resulted in both gelation and creaming; maintaining the alcohol level but decreasing the total solids to 37·5% increased emulsion stability, but the storage life at 45 °C was only a few days. Again, both creaming and gelation were observed. These results suggested that a commercially viable product could be made at 42° proof, but only by decreasing the total solids content, with consequent effects on the texture of the product and its mouthfeel.

However, by using a relatively minor variation in the manufacturing process (see Fig. 1) it proved possible to produce a cream liqueur containing 42° proof alcohol and 40% total solids and having a satisfactory stability, i.e. able to withstand storage at 45 °C for at least 30 days. In essence, the variation involved making a liqueur of slightly higher solids content than required finally, but at the usual proof (30°), and subsequently diluting the cooled product with neutral spirit to achieve the desired total solids and alcohol contents. The stabilities of products made in this manner as a function of alcohol and solids levels are recorded in Table 1.

Emulsion stability is obviously a function of both the alcohol content and the proportion of solids. In fact, the principal determinant of instability was the alcohol content of the liquid phase, as can be seen from Fig. 3. For example, there was little difference in the ethanol content of the liquid phase of a 45° proof liqueur containing 35% solids and that of a 42° proof emulsion with 40% solids, and both have similar stabilities.

Emulsion breakdown in liqueurs with the lower proportions of ethanol in the liquid phase was due overwhelmingly to serum separation. However, as the proportion of ethanol in the liquid phase rose, serum

TABLE 1
Effect of Alcohol Content and Total Solids Concentration on Stability of Cream Liqueur Stored at 45 °C

Alcohol strength (° proof)	*Emulsion stability (days)*[a]		
	Total solids (%)		
	35·0	*37·5*	*40·0*
30	>110	>110	>110
33	>110	>110	>110
36	115	102	98
39	83	77	61
42	53	50	34
45	35	20	15

[a] Emulsion stability = days at 45 °C until visible separation of serum.

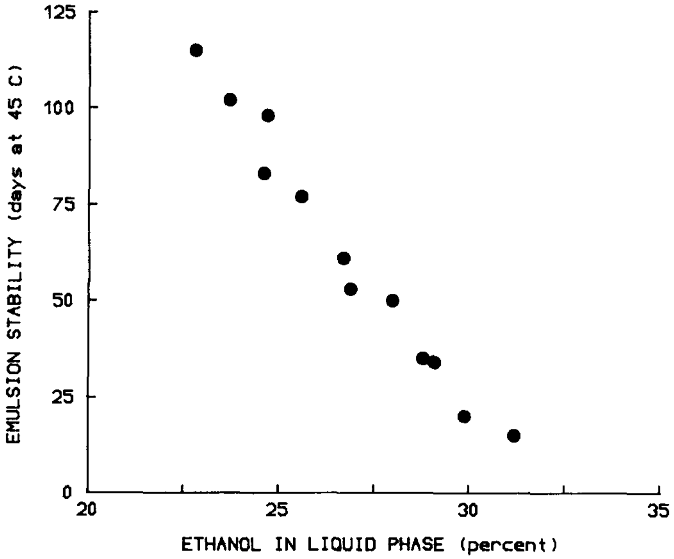

Fig. 3. The relationship between emulsion stability and ethanol content of the liquid phase of liqueurs.

separation was increasingly accompanied by creaming. In samples stored at ambient temperatures, creaming became apparent after storage for a few months, manifesting itself as a deposit on the glass surface at the liqueur/air interface. The defect was largely cosmetic, since, even in the neck of a bottle, the aggregate did not prevent free flow of the liqueur (after prolonged storage). Nevertheless, it was thought appropriate to investigate the nature of the creaming process.

The nature of the creaming process

The viscosities of the various cream liqueurs described in Table 1 are recorded as a function of alcohol content in Fig. 4. Viscosity was, as expected, highly dependent on the concentration of solids, but at each total solids level there was a marked rise in viscosity as alcohol content increased beyond 39° proof. It is, of course, well known that significant changes in viscosity occur as alcohol is added to aqueous systems. To

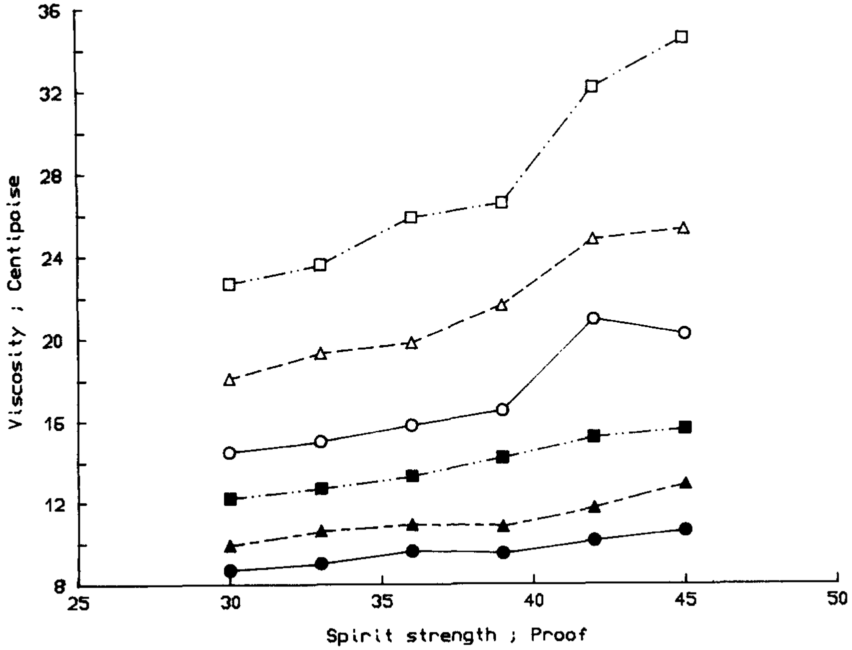

Fig. 4. The relationship between spirit strength and viscosity for cream liqueurs. □, 40% total solids; △, 37·5% total solids; ○, 35% total solids and for sugar solutions; ■, 40% total solids; ▲, 37·5% total solids and ● 35% total solids.

demonstrate the extent of such changes, model systems in which the solids component was entirely sucrose were produced, and their viscosities as a function of alcohol content are also recorded in Fig. 4.

Comparison of the cream liqueur with the model system emphasises the large contribution of the fat and protein present in the former system to the viscosity. The different behaviour of the two systems also demonstrates, quite unambiguously, that the increase in viscosity of cream liqueurs at high alcohol contents is not due to water/ethanol interaction. Rather, the increase must be due to response of the homogenised system to increasing amounts of alcohol. The observations are consistent with some type of incipient aggregation occurring.

Support for that contention was obtained using the Coulter Counter (see Fig. 5). The proportion of particles having diameters greater than 0·5 and 1·0 μm increased with alcohol concentration, the effect becoming particularly marked when the proof exceeded 39 °. Since the entire series

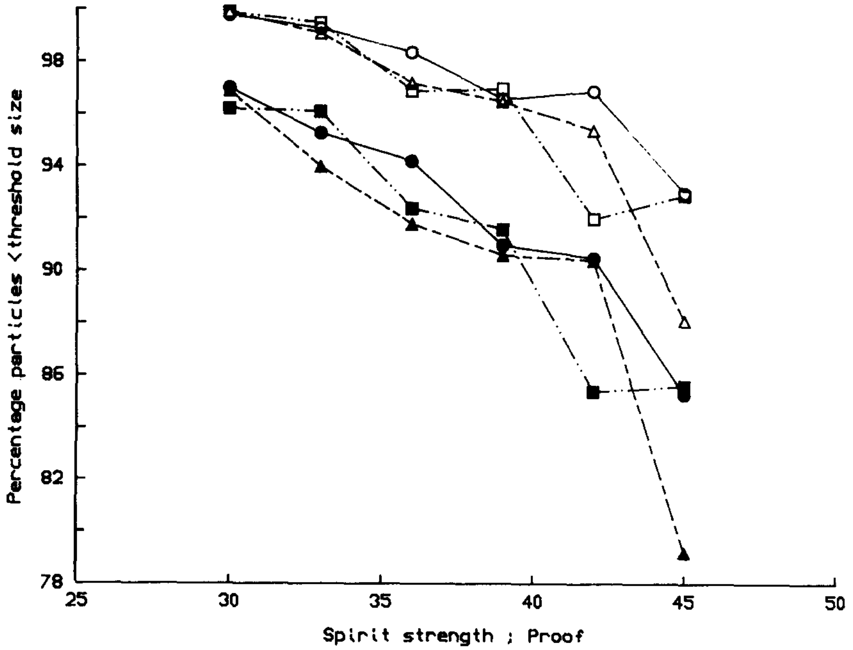

Fig. 5. The relationship between the weight fraction of large particles in the emulsion and the ethanol content. Particles (weight per cent) less than 0·5 μm, ■, 40 % total solids; ▲, 37·5 % total solids; ●, 35 % total solids; particles (weight per cent) less than 1 μm, □, 40 % total solids; △, 37·5 % total solids; ○, 35 % total solids.

of liqueurs had been made by the addition of alcohol or alcohol and water to a single batch of cream liqueur made at 30° proof (see Fig. 1), the aggregation was a specific result of that final addition of alcohol.

The results of these physical measurements are therefore consistent with the occurrence of some type of aggregation taking place as a consequence of increasing alcohol concentration. Very little change in the state of aggregation was recorded over prolonged storage periods at ambient temperature. Only when failure due to serum separation and creaming was imminent did viscosity increase massively.

The fact that high proof cream liqueur possessing commercially viable emulsion stability could not be made by the standard process whilst a relatively minor variation of that process greatly increased stability suggested that there were interactions between the composition of the liqueur and processing conditions that led to aggregation. This area was therefore further investigated.

The cause of creaming

We have now shown that a cream liqueur of, for example, 40% total solids and 42° proof is subject to an incipient aggregation process that eventually leads to emulsion breakdown, expressed as serum separation and creaming. The two defects appeared to be related and, since we have previously shown (Banks *et al.*, 1981*b*) that serum separation in cream liqueurs at 30° proof is catalysed by ionic calcium, the possibility arose that the sequestrant (citrate) of ionic calcium was not performing satisfactorily at higher alcohol levels. Recourse was therefore made to a more powerful sequestrant—sodium hexametaphosphate.

Cream liqueur (40% total solids and 45° proof) was prepared by the standard procedure, but omitting stabiliser, rather than the variation described above. The liqueur was divided into ten portions, to five of which citrate was added at levels of 0–8 mM/litre, whilst, to the remaining five samples, corresponding amounts of sodium hexametaphosphate were added. These samples were then subjected to the usual assessment of emulsion stability and the results are recorded in Table 2.

Emulsion stabilities were effectively the same in the two series, showing that no advantage accrued from using a stronger calcium sequestrant. More important, however, was the observation that, with both sequestrants, emulsion stability decreased with increasing level of addition. Thus, although the cause of instability in high proof cream

TABLE 2
Effect of Adding Calcium Sequestrant to Cream Liqueur (45° Proof) After Formulation

Sequestrant	*Emulsion stability (days)*[a]				
	Level of addition of sequestrant (mM/litre)				
	0	*1*	*2*	*4*	*8*
Trisodium citrate	10	2	2	1	1
Sodium hexametaphosphate	10	4	2	1	1

[a] Emulsion stability = days at 45 °C until visible separation of serum.

liqueurs cannot be associated with ionic calcium *per se*, it does appear to be associated with the presence of ions.

Liqueurs made with washed cream and butteroil

The inorganic material in cream liqueurs originates from three sources—the cream itself, sodium caseinate and stabiliser (usually trisodium citrate). However, the stabiliser is added to sequester calcium ions present in the cream. Hence, if inorganic material is removed from the cream, there is no need to add stabiliser and the only ions present in the final product come from the sodium caseinate. The removal can be accomplished easily, either by washing the cream (Fig. 2) or by using butteroil as the starting material. Both these techniques have previously been shown to be effective in increasing emulsion stability in liqueurs at 30° proof (Banks *et al.*, 1981*b*).

From these starting materials, liqueurs containing 40 % solids and 36° to 45° proof spirit were prepared, using the standard procedure, i.e. homogenisation was carried out in the presence of the amount of alcohol in the final product. The stabilities of the resultant emulsion were measured by storage at 45 °C and the results are shown in Table 3.

With washed cream, it was possible to prepare a 42° proof product that did not exhibit emulsion instability on storage at 45 °C until 38 days had elapsed; the same product made from whole cream showed instability on overnight storage at 45 °C. Hence, there can be no doubt that the components of cream present in the aqueous phase catalyse the reactions leading to the breakdown of the emulsion.

TABLE 3
Effect of Storage at 45 °C on Emulsion Stability of Liqueurs Made from Washed Cream or Butteroil

Sample[a]	*Emulsion stability (days at 45 °C)*			
	Spirit strength (° proof)			
	36	*39*	*42*	*45*
Washed cream	> 100	92	38	13
Washed cream + citrate[b]	> 100	40	15	8
Butteroil	> 100	75	16	6

[a] All samples had 40 % total solids.
[b] Trisodium citrate was added at 10 millimoles per litre of product.

Using butteroil, the product liqueurs were more stable at higher alcohol contents than those made with whole cream, but less so than those made with washed cream. This phenomenon was highly reproducible, suggesting that the milk fat globule membrane material present in washed cream may contribute an additional stabilising effect at the high alcohol contents.

The addition of trisodium citrate to the system containing washed cream decreased shelf-life in liqueurs of 39° proof and above. This observation supports the contention that ionic material is a cause of emulsion instability at these high alcohol contents.

In addition to serum separation, samples of high alcohol content also showed creaming on failure in the accelerated storage trial. Hence, the latter phenomenon appears to be associated with alcohol content (or lack of water). However, at ambient temperature the visible signs of creaming within the bottle were decidedly less when the liqueur was made from washed cream by the conventional manufacturing process than from whole cream using the variant procedure.

Physical properties of liqueurs made from washed cream

The viscosities of liqueurs made from washed cream, washed cream plus 10 mM citrate and whole cream plus 10 mM citrate are shown in Fig. 6. It should be noted that the first two of these products were made by our standard procedure (Banks *et al.*, 1982) whilst the third was made by the

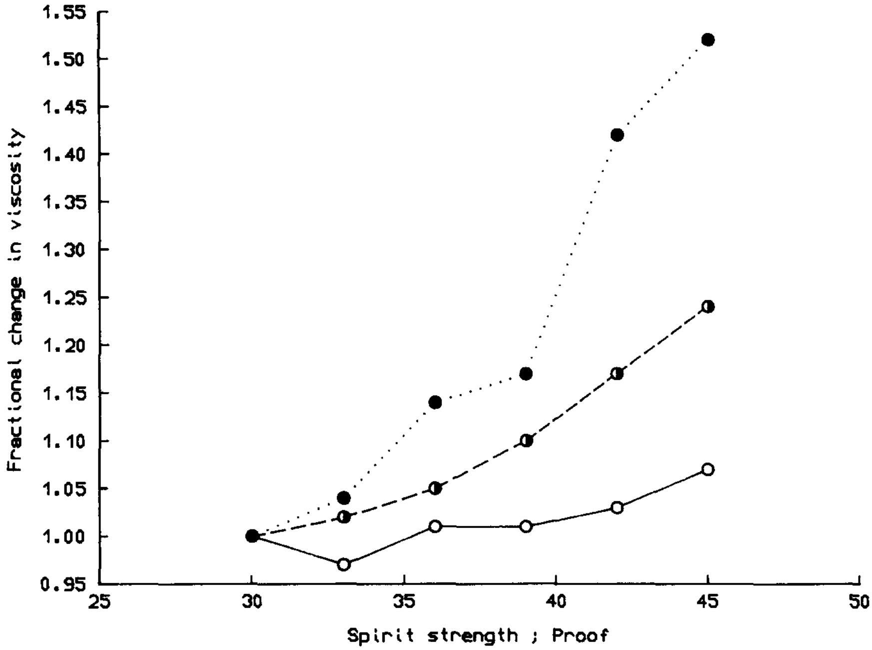

Fig. 6. Fractional change in viscosity with increasing alcohol strength for liqueurs containing 40% total solids made by the single-stage method of Banks *et al.* (1982). ○, washed cream; ◑, washed cream + 10 millimoles added citrate per litre. For comparison, values (●) are also shown for cream liqueurs + 10 millimoles added citrate per litre, containing 40% total solids made using the modified manufacturing sequence shown in Fig. 1.

variation of that procedure, described earlier (*cf.* Fig. 1). When using washed cream, it is necessary to amend the composition of the mix to take account of the lactose and protein lost in the washing. For that reason, the viscosities of products made from cream and washed cream are not directly comparable, and it is necessary to use relative values. In Fig. 6, the viscosity of the liqueur containing 30° proof alcohol is arbitrarily ascribed the value unity in each series and all the other values are given as multiples of these; all the liqueurs contain 40% solids.

With washed cream, there is very little change in viscosity, even at 45° proof alcohol. The addition of citrate to the washed cream leads to consistently higher viscosities as alcohol content increases. However, even adding citrate to the washed cream and then homogenising at the final concentration of alcohol produced liqueurs with lower relative viscosities than did the use of the variation in manufacturing process described above.

The proportions of particles exceeding 0·5 and 1·0 μm in the various liqueurs (see Fig. 7) followed the same general trend as did the viscosities. Thus, a relatively small change was observed in the proportion of large particles with increasing concentrations of alcohol when washed cream was used as the starting material. The proportions were slightly, but consistently, higher as the alcohol content increased when washed cream and 10 mM citrate constituted the raw material. At proof levels of 39 ° and above, the highest proportions of large particles were associated with the use of the whole cream and the modified manufacturing process shown in Fig. 1.

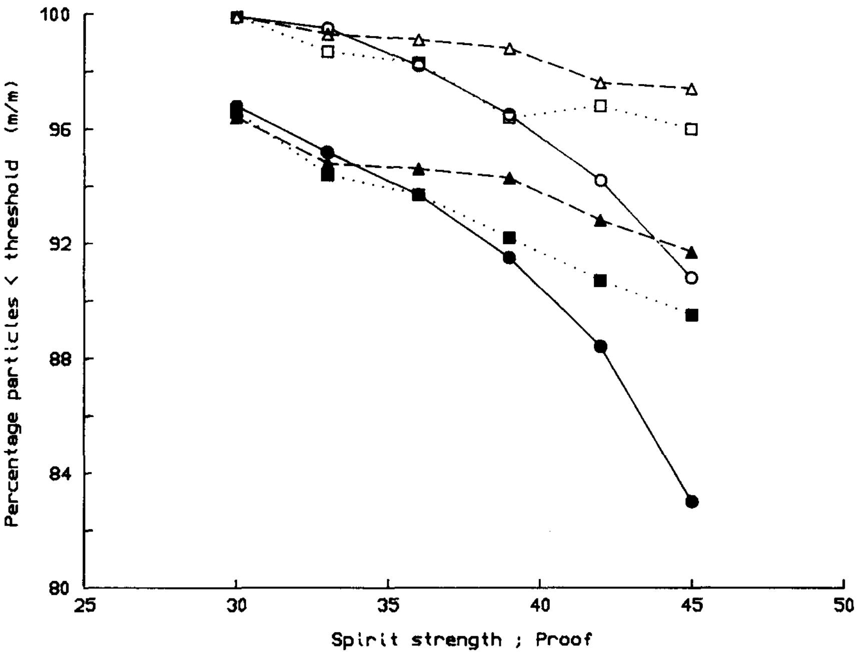

Fig. 7. The relationship between the weight fraction of large particles in the emulsion and the ethanol content; closed symbols refer to particles over 0·5 μm and open symbols to those over 1·0 μm. Liqueurs made by the single-stage method of Banks *et al.* (1982) using washed cream (△▲) and washed cream + 10 millimoles added citrate per litre (□■). For comparison, values (○●) are also shown for cream liqueurs containing 40 % total solids made using the modified manufacturing sequence shown in Fig. 1.

CONCLUSION

The object of this work was to produce cream liqueur containing 40% solids and 42° proof alcohol. We have now shown that this may be achieved in two ways—either by using whole cream and modifying the manufacturing process or by using washed cream and the normal manufacturing process. The latter approach is better in terms of there being less incipient aggregation, as shown by viscosity and particle size measurements, and in producing a marginally more stable emulsion (compare the relevant values in Tables 1 and 3). However, the individual manufacturer must make the choice.

It is interesting that, starting from cream, a stable emulsion cannot be made directly at high alcohol contents, but rather must result from the separate addition of neutral spirit. Emulsions made in both ways should have identical chemical compositions—hence, some destabilising reaction must occur during processing at these high alcohol levels. That reaction is apparently catalysed by one or more of the serum components of the cream. A single washing of the cream, which produces a *ca.* six-fold decrease in the concentration of serum components, did not lead to suitable emulsion stability, e.g. at 40% solids and 42° proof, the emulsion was stable for only 18 days at 45 °C.

There remains the possibility that the ionic materials that obviously catalyse emulsion breakdown during storage at 45 °C (see Table 2) are not necessarily those involved in the destabilisation that occurs during processing at high alcohol levels. This area is currently being investigated.

ACKNOWLEDGEMENTS

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