Colloids and Surfaces A: Physicochem. Eng. Aspects 352 (2009) 38–46

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Stability of alcoholic emulsions containing different caseinates as a function of temperature and storage time

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ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form
24 September 2009
Accepted 26 September 2009
Available online 8 October 2009

Keywords:
Alcohol
Caseinate
Flocculation
Emulsion rheology
Particle size distribution
Cream liqueur

ABSTRACT

Alcoholic emulsions were prepared with three different caseinate batches at 3 and 4% (w/v) protein content and 16.9% (v/v) ethanol content. Two storage temperatures (25 and 40 °C) and three storage times (0, 25 and 45 days) were used. The rheological behaviour and particle size distribution of samples were obtained. The caseinate batches #106 and #102 stabilized the emulsion up to 45 days storage time. While emulsions prepared with caseinate batch #103 never achieve stabilization. Stability of the emulsion was also proven by adding ethanol and visually detecting coalescence, the protein content showed to be crucial to reduce coalescence, for all emulsions with 4% protein content, coalescence visually appeared at higher alcohol content than for emulsion with 3% protein content. For the emulsion prepared with caseinate batch #103, coalesce was detected at the lowest alcohol concentrations (<30%), while for emulsion prepared with caseinate batch #102 coalescence was detected at the highest alcohol concentrations (>40%) this effect was consistent with the inverse of ions content. Viscosity was found to increase with storage time in all the blends. The volumetric diameter (4,3) was a function of storage time and in all cases the coalescence increases.

1. Introduction

In the food industry, emulsions play an important role in the preparation of several products such as salad dressing, catsup, Dijon mustard, etc. In the field of food additives, alcoholic cream liqueurs emulsions are of special interest. The stability and shelf life of these emulsions depend on several factors such as viscosity, volume particle size, temperature, pH, ionic forces. Commonly the effect of caseinates is underestimated, for example, the content of Ca^{++} and Na^{+} in caseinates influences the stability of alcoholic emulsions.

Caseinates are commonly used as an additive in the food industry for water binding, fat binding, viscosity modification, whipping agent, and emulsion stabilizer [1,2]. This ingredient is found in a wide variety of food products such as coffee, whitener, drinking chocolate, yoghurt, and meat products. Depending on the product, the caseinate content can range from 1 to 4% (w/v). A commercial use of caseinates is as emulsifying agent in alcoholic cream liqueurs [3]. Cream liqueurs of about 15% alcohol content can be prepared with an extended shelf life of several years.

The presence of alcohol (ethanol) can confer increased stability by reducing interfacial tension between oil and aqueous phases and thus producing a lower average droplet size during emulsification. Additional ethanol ultimately leads to emulsion destabilization through collapse of the steric layer and increased sensitivity to electrolytes, and subsequently to protein-coated droplet precipitation [4,5]. The latter process involves diffusion of oil through the aqueous continuous phase leading to the growth of large oil droplets at the expense of smaller ones. This is enhanced by reduction in solvent polarity (dielectric constant) on addition of alcohol [4,5].

Experiments on the effect of alcohol concentration on the stability of model emulsions containing sodium caseinate as the primary emulsifier, have shown that over a certain critical alcohol concentration (30–40 wt%, depending on protein content in calcium caseinate), the systems become very unstable [6,7]. Protein precipitation and droplet aggregation take place because the aqueous phase with high content of ethanol is a poor solvent for the protein [8]. At alcohol concentrations close to the protein solubility limit, the decrease of solvent quality causes a reduction in the surface tension, reducing the steric stabilization [2,9]. The addition of alcohol also causes a reduction in the dielectric constant and has a negative influence to any electrostatic stabilization mechanism [10].

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doi:10.1016/j.colsurfa.2009.09.046

At alcohol levels quite below the concentration that causes protein precipitation, the addition of ethanol can actually enhance emulsion stability, because ethanol causes a significant reduction in the interfacial tension between the oil and the continuum phase containing the protein in solution [8]. Hence the homogenization of a premixed emulsion containing alcohol produces oil droplets with significantly lower average size (i.e. <5 μm) than the equivalent alcohol-free systems [10].

Studies on emulsions with alcohol and caseinate where protein concentration is considerably higher than the required for saturation coverage of droplets, showed an enhancement of the emulsion stability [11]. This was attributed to the presence of unabsorbed protein particles in the aqueous phase [12]. The depletion occurs in a manner rather similar to that observed in emulsion systems containing small-molecule surfactant micelles [13,14]. This work explores the effect of several kinds of commercial caseinates and their mixtures into the stability and shelf life of alcoholic cream liqueurs as estimated by rheological and volume particle size distribution (PSD) behaviour at different storage times and temperatures.

2. Materials and methods

Spray dried commercial caseinate (90 wt% protein) from three different batches (batches #102, 103 and 106) from LACTOPROT, S. A. (Kaltenkirchen Laboratories, Germany), were used without further purification. A sample of spray dried sodium caseinate and their metallic ion content was recorded as shown in Table 1; the analysis was supplied by Kaltenkirchen Laboratories, (Germany). An initial aqueous phase containing 16.9% of neutral alcohol was prepared according to formulation (Table 2) by Lynch and Mulvihill [15].

2.1. Emulsion preparation

Oil-in-water emulsions were prepared using caseinate as the emulsifier agent. Caseinates with variable metallic ion content were used (Table 1). A GEA-NIRO Mod 2652 homogenizer was used at high-pressure (250 bar) and 55–60 °C for emulsions preparation. Homogenization times were adjusted to ensure an equivalent average droplet diameter for all emulsions regardless of alcohol content, $d(4,3)$. In this work, the cream liqueur was prepared following a procedure (Table 3) originally proposed by Lynch and Mulvihill [15]. Once the alcohol and oil emulsions have been prepared separately, mixing of these two emulsions follows two-stage process: in the first stage, the liqueur cream base was premixed applying mechanical agitation by means of a Rotor–Stator system at 1500 rpm and 65–70 °C by 10 min. In the second stage, the liqueur cream base was premixed under the same agitation conditions as stage one but at lower temperature (45–55 °C) by another 10 min. Then, the pre-emulsion was prepared by mixing using the Rotor–Stator system at 2000 rpm – 20 min at 40 °C and finally it was homogenized in the homogenizer GEA-NIRO (USA). The cream liqueur was bottled and pasteurized in a water bath at 90–95 °C for 20 min, followed by cooling with cold water and then analyzed.

Table 1
Metallic ion content in caseinate batches #102, 103 and 106.

Caseinate batch #	Ca^{++} (ppm)	Na^{+} (ppm)
102	0.521	9.42
103	0.505	14.14
106	0.479	12.85

Table 2
Formulation of cream liqueur [15].

Materials	% (w/w)
Water	43.50
Refined sugar	19.00
Neutral alcohol, spirit (bp 80°)	16.90
Butyric fat	15.50
Calcium caseinate	3.08
Glyceryl monostearate	0.34
Citrate trisodium	0.16

Table 3
Premixing stages for liqueur cream preparation.

Stage 1, 25 °C	Stage 2, 45 °C
Water (80%)	Water (20%)
Citrate trisodium	Refined sugar
Butyric fat	Neutral alcohol, spirit (bp 80°)
Glyceryl monostearate	
Calcium caseinate	

2.2. Caseinate dispersions

Alcohol-free caseinate dispersion samples (20 mL) having different protein contents (3 and 4% (w/v)), were titrated with absolute ethanol under constant agitation and temperature of 25 °C until visible coagulation was observed. A small amount of ethanol (1 mL) was added each time using a lab burette. The wall glass of reservoir was observed for the first visible coagulated particles. The initial and apparent pH were recorded and monitored systematically during titration using a commercial pH meter previously calibrated (model Bench top pH-meter, Term Orion, USA). Turbidity of caseinate dispersion could also be monitored during titration reading the absorbance at 600 nm (visible light) as an estimation of aggregation. A commercial spectrophotometer was used to measure the absorbance (model Genesys 10 UV Scanning Spectrophotometer, USA) [3,9].

2.3. Cream liqueurs preparation with different mixtures of commercial caseinate batches

Cream liqueurs were made with different mixtures of commercial caseinate batches (i.e., #102 and 106) at the following fixed content ratios: 20/80, 60/40 and 40/60 (w/w%). These mixtures were prepared following the same formulation from Table 2.

2.4. Rheology measurements

Preparation of emulsion for viscosity measurements was as follows: 70.3 g of a caseinate batch without alcohol (about 67.5 g of dry matter) was weighed in a 600 mL beaker (weight A, g) and cold water (379.7 g) was slowly added using a Rotor–Stator system at 300 rpm – 20 min at 25 °C. The mixture was stored for 12 h at room temperature to stabilize and to allow for lumps to be moistened. Then the beaker with its contents was placed in a water bath at 70 °C for 30 min under occasional stirring to keep a homogenous solution. After dissolving, the mixture was completed to the initial weight (A + 450 g) to compensate for evaporated water, cooling the beaker under running water at 20 °C for 4 h. The rheological measurements were performed on a strain-controlled rheometer TA Instruments Rheometer (model AR2000, UK) using a double concentric geometry. The viscosity was measured at different storage times and temperatures (0, 15, 30 and 45 days, 25 and 40 °C, respectively). The samples at 0 days storage time were given 40 min of stabilization time after preparation. The emulsions were characterized under unidirectional steady shear and oscillatory flow. The storage G' and loss G'' *moduli* were determined through small amplitude oscillatory shear flows at frequencies ranging from 1 to 400 rad/s

at different temperatures and three storage times, under linear viscoelastic conditions. From strain sweep runs, the upper limit of the linear viscoelastic zone was located at strain of about 0.50. In this domain, the experimental tests are essentially nondestructive and can be interpreted in terms of the molecular structure of the material [16]. All tests were carried out at least by duplicate.

2.5. Particle size distribution (PSD)

The PSD of emulsions were measured using a laser diffraction analyzer in aqueous medium (Malvern MasterSizer model 2000 S). Refractive index of 1.400 and 1.330 were used for the emulsions and the reference (water, 1.33), respectively. The volumetric diameter $d(4,3)$ was analyzed as well as the specific superficial area (SSA, m^2/g) at different conditions of storage. The average volume–surface droplet diameter for each freshly made emulsion was set in the range of 0.1–5.0 μm and then analyzed. All tests were carried out at different temperatures (25 and 40 °C) and at three storage times (0, 25 and 45 days). The PSD tests were made by duplicate.

2.6. Microscopy

Microphotographs were obtained with an OLYMPUS BX45TF (Olympus Optical Co. Ltd., Tokyo, Japan) microscope equipped with a 30 W lamp (390–420 nm wavelengths reflected light), at 100×. The images from microscopy were analyzed to obtain information regarding the morphology of the emulsions prepared with different types of caseinates.

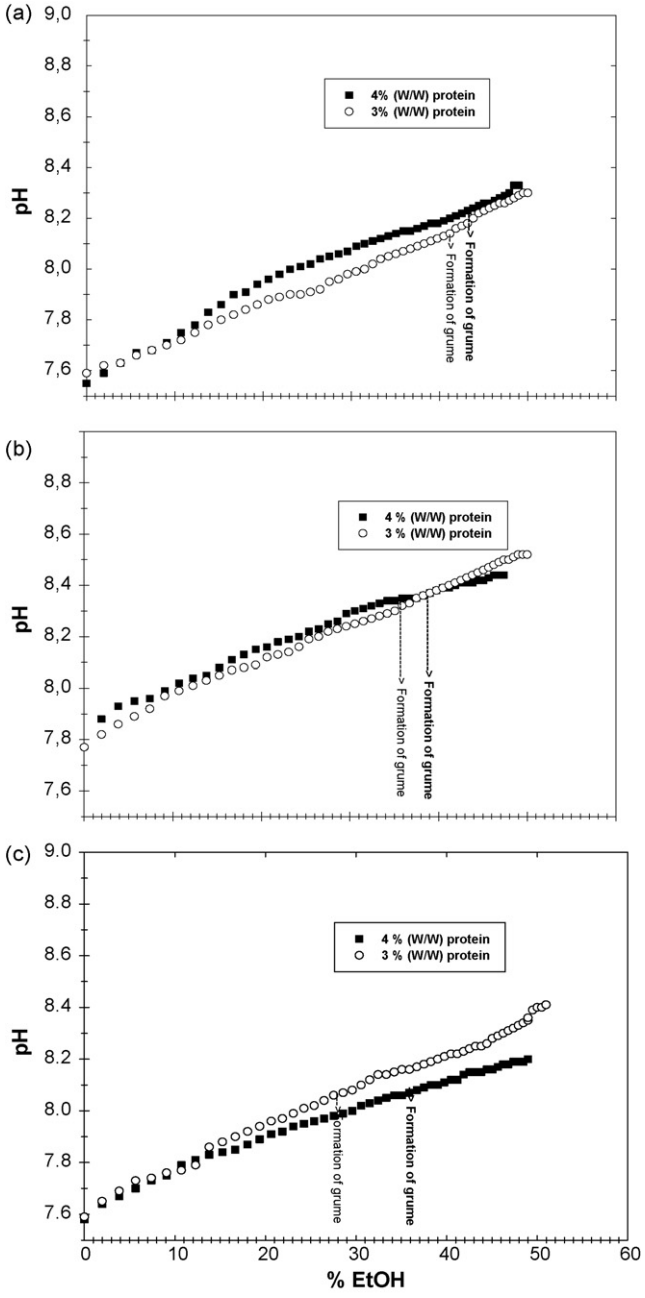

Fig. 1. Stability to ethanol at different protein concentration (a) batch #102, (b) batch #106, (c) batch #103.

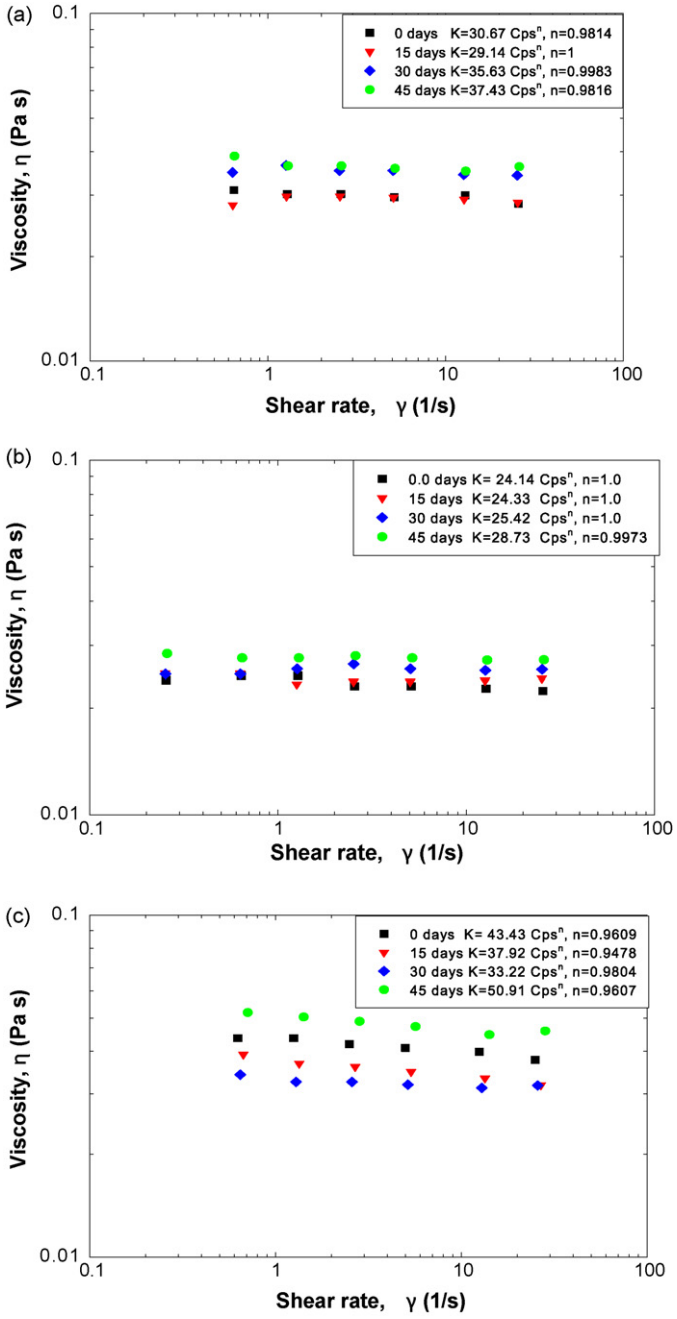

Fig. 2. Viscosity of prepared emulsions at different storage periods at 25 °C up to 45 days: (a) batch #102, (b) batch #106, (c) batch #103.

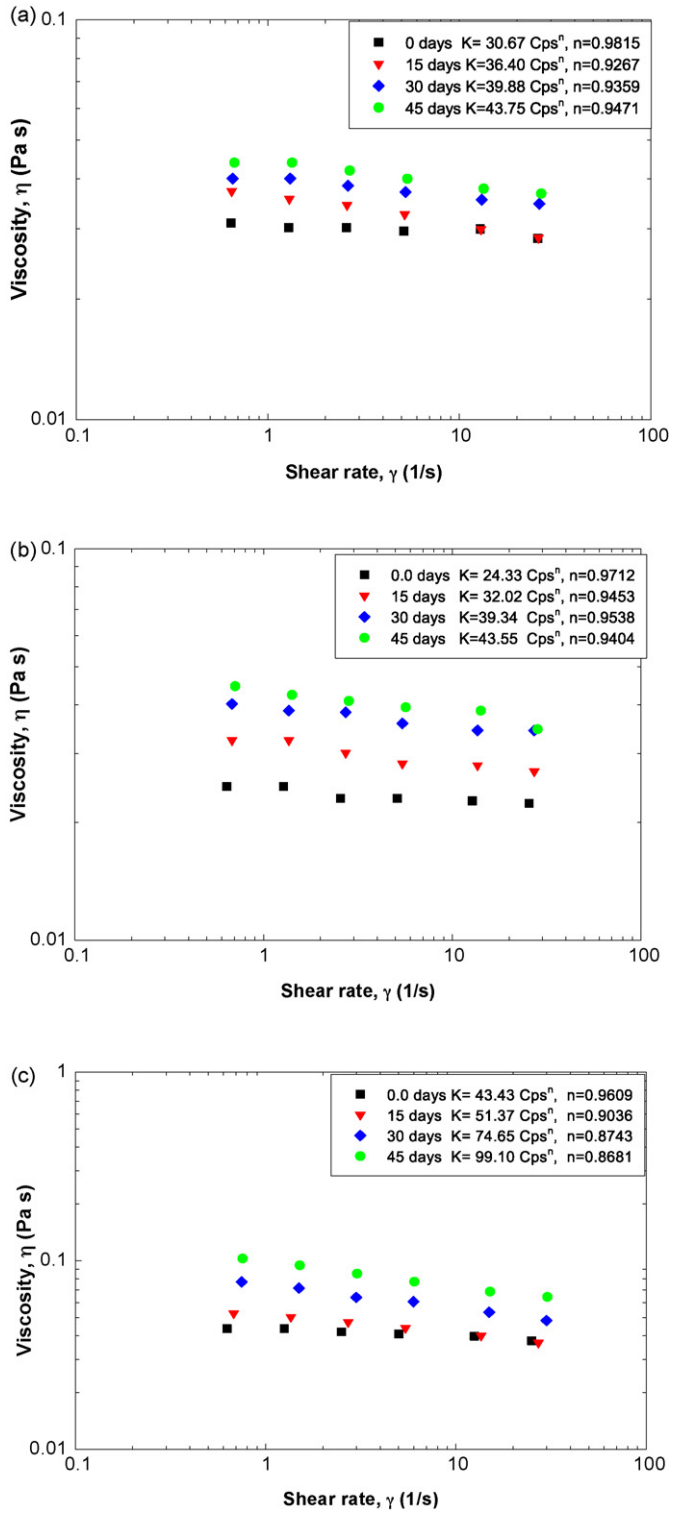

Fig. 3. Viscosity of prepared emulsions at different storage periods at 40 °C up to 45 days: (a) batch #102, (b) batch #106, (c) batch #103.

3. Results and discussion

The effect of alcohol addition on the stability of caseinates emulsions at protein concentrations of 3 and 4% (w/v) is shown in Fig. 1. Results show that caseinate emulsions with low protein content (3%) coalesce at lower alcohol contents than emulsions with higher protein content (4%). For the emulsion prepared with batch #103, visible coalescence appeared at the lowest alcohol concentration

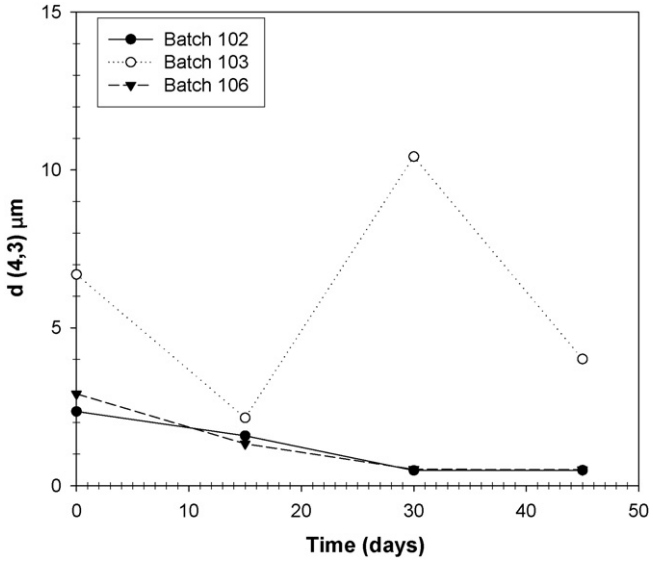

Fig. 4. Particle diameters of alcoholic emulsions at 25 °C by 45 days.

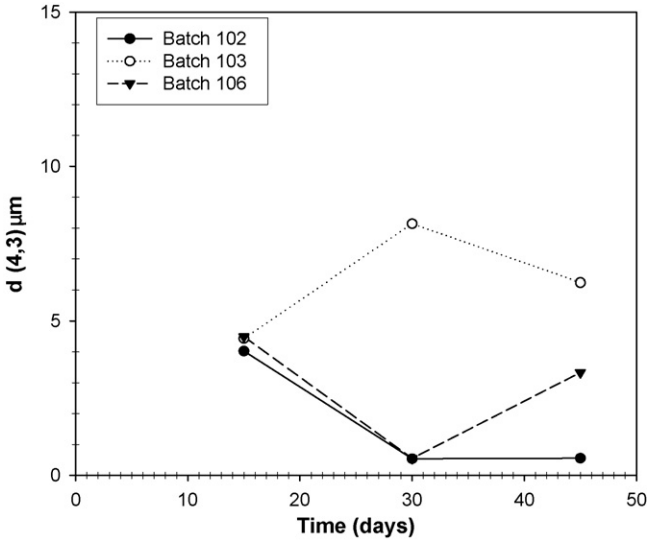

Fig. 5. Particle diameters of alcoholic emulsions at 40 °C by 45 days.

(<30%) and pH (at 8 pH aprox) while the emulsion containing caseinate batch #102 probed to be the most stable (i.e. visible coalescence appeared at no less than 40% alcohol content), these results show that the ethanol content plays an important role in the stability of this type of emulsions, since results also show that emulsion stability is consistent with the total ion content ($Na^+ + Ca^{++}$) being batch #103 the caseinate with the highest total ion content and batch #102 that with the lowest (Table 1). The pH value at which flock formation was detected was also found to be directly related to the total ion content in the final emulsion.

It is important to note that pH increases consistently with the alcohol content and the relation pH-alcohol seems to be independent of the protein content except for batch #103 where the system with 4% protein content shows lower pH values than that for 3% protein content at the same alcohol content. This indicates that the flocculation/coalescence mechanism is different for the systems with low total ion content (batches #102 and #106).

In the experimental samples (#103), the flocculation was substantially enhanced by sodium and calcium present in the caseinate emulsions, similar behaviour was observed by Golding [17] and Ye

and Singh [18]. It is now rather well established that fine oil droplets coated with caseinate at saturation surface coverage are extremely stable towards coalescence at neutral pH 7.0 [8,12]. In this work the initial pH of emulsion was no less than to 7.5 at different ionic strength (i.e. $Na^{+} + Ca^{++}$ content); droplet emulsions containing alcohol are reported to be stable even under flow conditions [19].

On the other hand, the rheological properties (shear flow steady-state viscosity) of the emulsions were evaluated. Emulsions were prepared with a setup protein concentration of 4 wt% and then added in the cream liqueur base formulation (Table 2). The addition of alcohol into the aqueous phase was variable but never more than 30% v/v. Emulsions prepared with caseinate batches #102 and #106 (Fig. 2a and b) showed Newtonian behaviour at all storage times while batch #103 (Fig. 2c) always followed power–law behaviour, this being more evident at 40 °C (pseudoplastic index, $n = 0.8$) (Fig. 2). At 25 °C minor changes in viscosity were observed for emulsions prepared with caseinate batches #102 and #106 with storage time while for batch #103 viscosity first decreased with storage time at 15 and 30 days and then viscosity increased at 45 days surpassing that at 0 days storage time. This apparently erratic behaviour seems to be related to the particle size distribution (PSD) as showed in Fig. 4 where particle size stabilization is observed for batches #102 and #106 after 30 days storage time while for batch #103 particle size stabilization is never achieved.

At 40 °C (Fig. 3), the viscosity curves for all emulsions follow Newtonian behaviour just after preparation (0 days) and then the behaviour becomes power-law after storage (at 15 and 30 days) (Fig. 3), this could be related to the particle size, since stabilization of the particle size at this temperature was never observed except for the batch #102 (Fig. 5). Viscosity in all cases increases consistently with storage time. As it was observed at lower temperature (25 °C) the greatest change in viscosity was again for batch #103, with viscosity being around 0.04 Pa s at 0 days storage time and 0.12 Pa s after 45 days at the same shear rate ($0.1\ s^{-1}$). Batch #103 probed to be the most unstable emulsion in steady shear flow at all storage times and temperatures tested, this is again consistent with the high ion content in the caseinate samples ($Na^{++}Ca^{++}$, see Table 1).

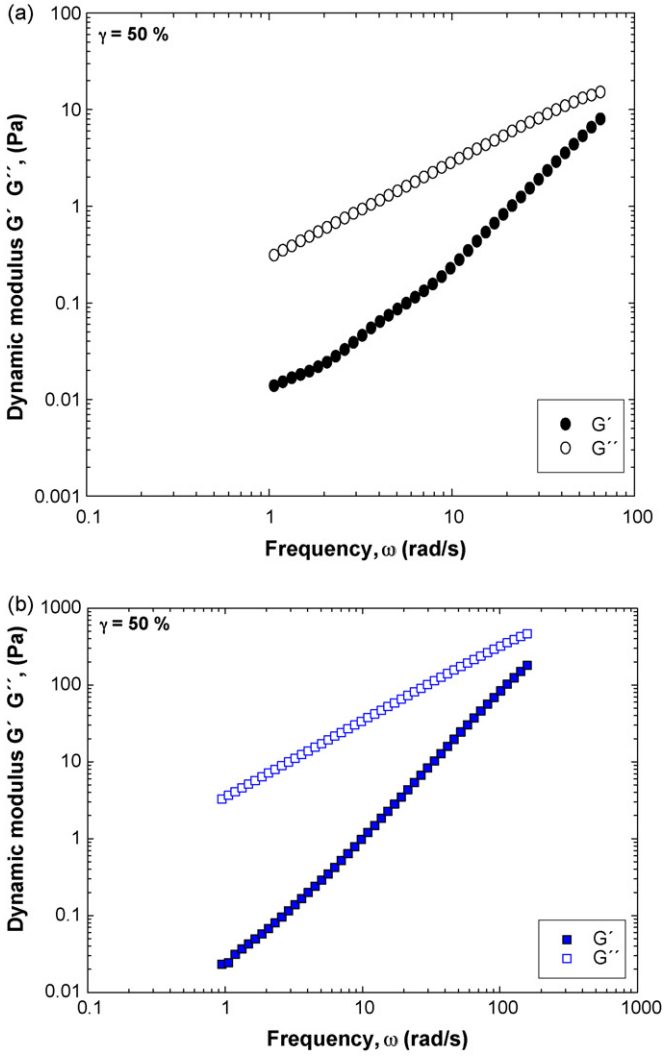

Fig. 6. Oscillatory flow curves for emulsions prepared with (a) batch #102 and (b) batch #103 at 45 days storage time.

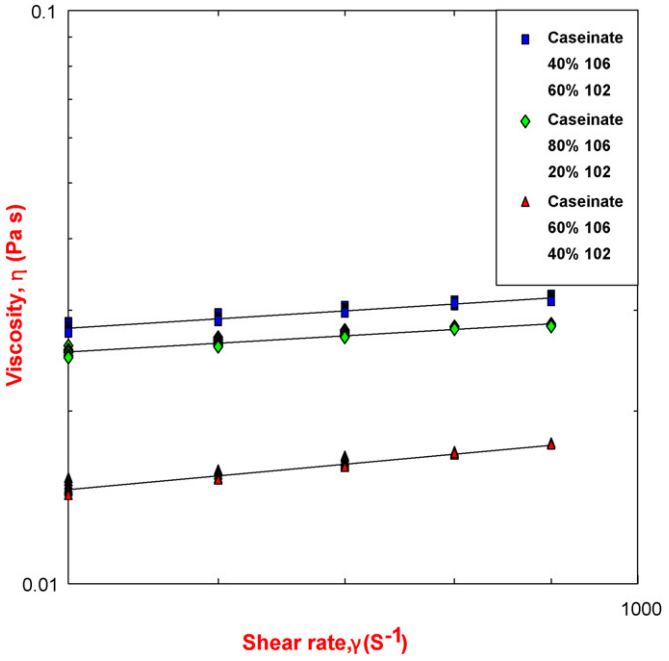

Fig. 7. Viscosity at shear rate in emulsions prepared with different commercial caseinates ratios at 25 °C by 45 days.

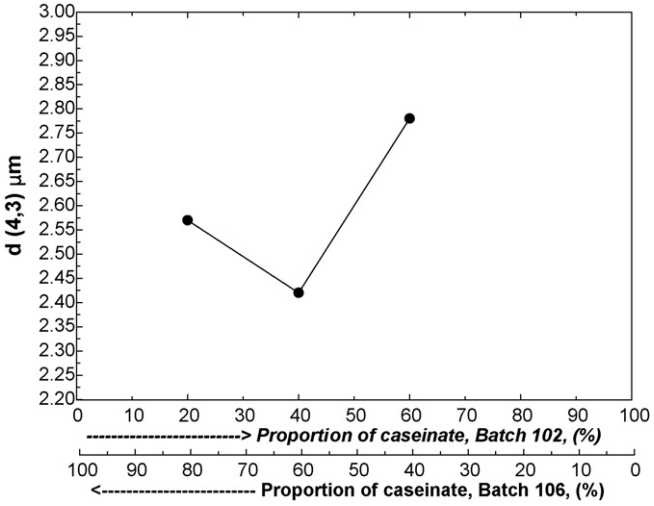

Fig. 8. Particle diameters of emulsions prepared with different commercial caseinates ratios at 25 °C by 45 days.

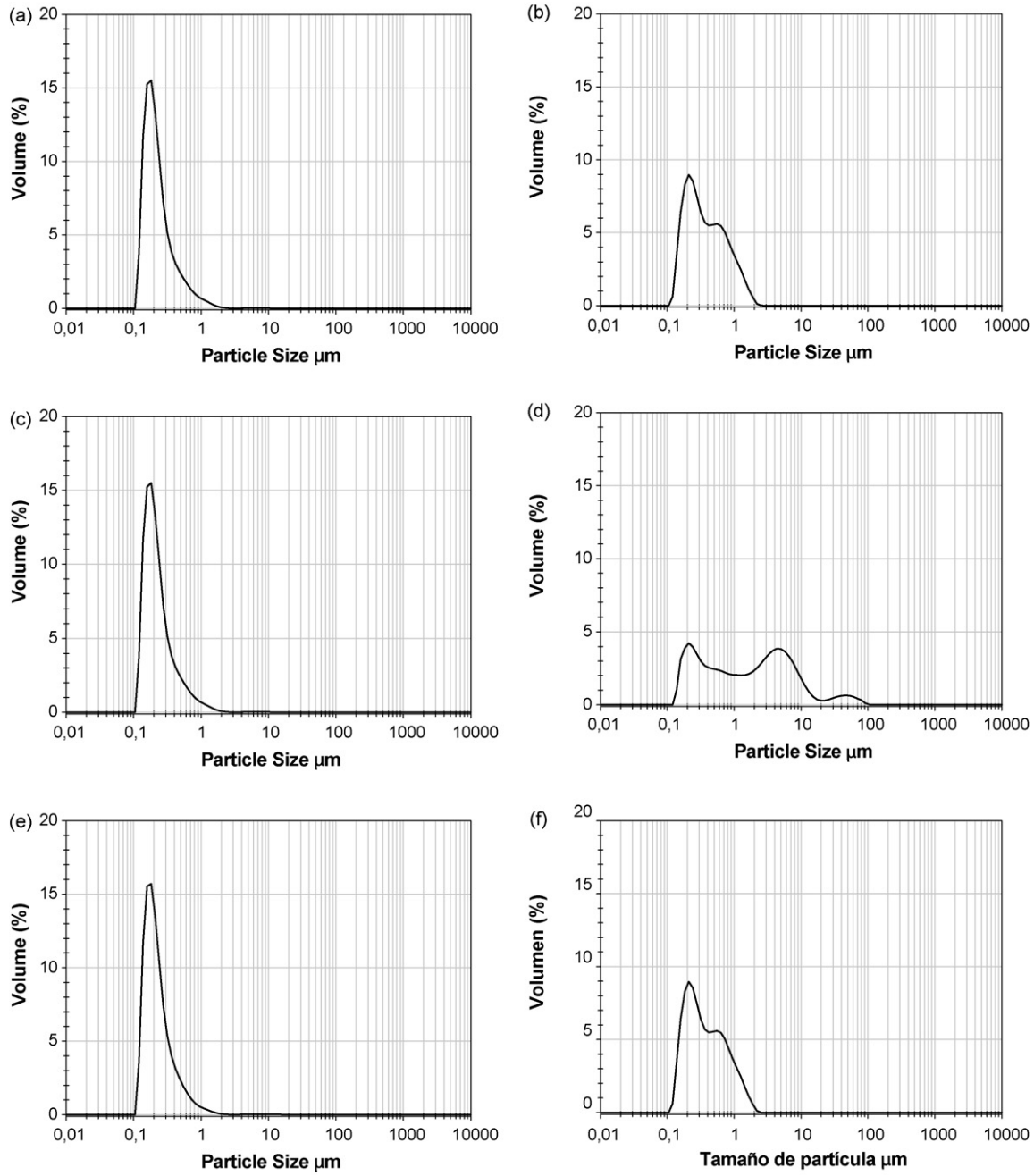

Fig. 9. Particle size distributions of alcoholic emulsions at 25 °C. (a) Batch #102, time 0, (b) batch #102, time 45 days, (c) batch #103, time 0, (d) batch #103, time 45 days, (e) batch #106, time 0, (f) batch #106, time 45 days.

High viscosity values for batch #103 are due to the high flocculation/coalescence observed in this system. In all cases, the results show changes in the PSD and rheological changes due to the effect of storage conditions, where batch #103 samples displayed a major increase in viscosity *vs*. storage temperature and time. Samples from batch #103 were more unstable than those prepared with other batches. This means that alcoholic emulsions at same storage time at both temperatures conditions and after the flocculation and coalescence have led to an immediate increase in viscosity reaching a maximum stable value, except for batch #103, which has shown a constant increase (Fig. 3). Thus the stability of this type of alcoholic emulsions was probably associated to their higher total ion content (Table 1). Same results were observed by Bos and Vliet [2], Ye and Singh [18], Bijsterbosch et al. [20], Dickinson and McClements [21], Krishnamoorti and Giannelis [22] and Murray [23].

Regarding viscoelasticity, Fig. 6 shows the results of the storage G' and loss G'' *moduli* as a function of frequency, the rheological behaviour of the emulsion with the batch #102 is different from that of emulsion with the batch #103. The evaluated materials showed a dependence with frequency $G' \alpha \omega^n$ ($n < 1$) which is a typical viscoelastic liquid behaviour rather than a viscoelastic solid. The terminal region of low frequencies is of special interest since the slope for caseinate batch #102 is significantly lower ($n = 0.35$, at low frequencies) than that for caseinate batch #103 ($n = 0.8$), this terminal slope (solid-like behaviour) is an evidence of a network like structure due to strong particle-solvent interactions (Fig. 6).

Fig. 7 shows the results on the stability of the oil thin layer formation for the emulsions prepared with different caseinate batches (#102 and #106) and different ratios (20/80, 60/40 and 40/60,

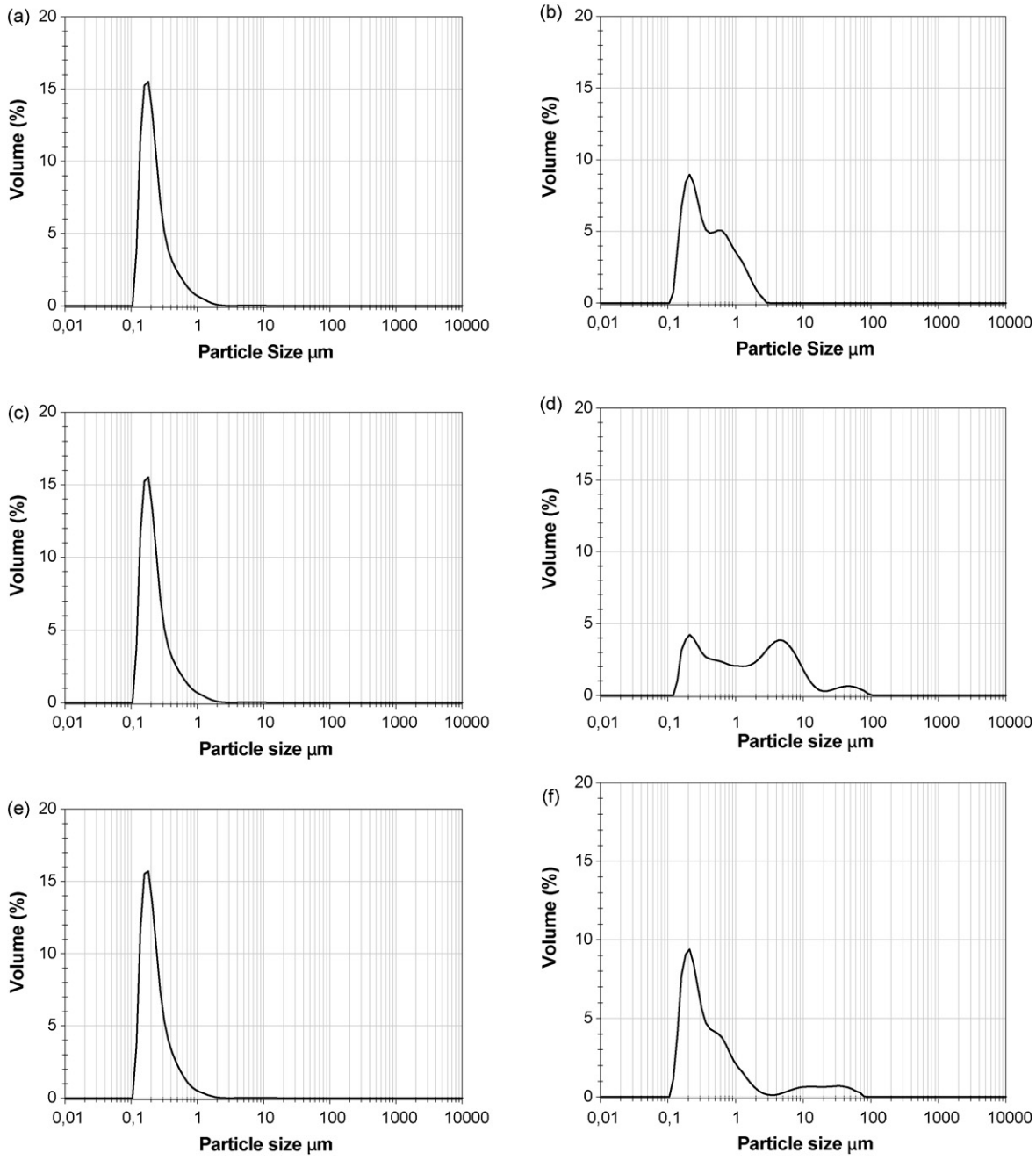

Fig. 10. Particle size distributions of alcoholic emulsions at 40 °C. (a) Batch #102, time 0, (b) batch #102, time 45 days, (c) batch #103, time 0, (d) batch #103, time 45 days, (e) batch #106, time 0, (f) batch #106, time 45 days.

w/w%) for 4 wt% protein-stabilized at 25 °C and 45 days. These emulsions were more stable at the final conditions (25 °C and 45 days). The only noteworthy change in emulsion behaviour caused by the caseinate ratios and the applied stored conditions was a minor change in solvent-protein interactions, attributed to protein quality and concentration variations in the caseinate batches used. These samples presented similar results in the rheological behaviour as fresh emulsions. It is noteworthy to note that the slope for these emulsions ($n > 1$) indicates a shear thickening system. This behaviour is typical of concentrated emulsions and in this case could be related to a instability in particle size (Fig. 8) and a change in PSD, results for $d(4,3)$ show that the distribution broadens for all samples after 45 days (Fig. 9). The negatively skewed one-modal size distribution after prolonged storage is indicative of destabilized emulsions by coalescence [2,24].

The particle size distribution in all emulsions has shown a one-modal distribution at the beginning of the experiment for each batch (#102, 103 and 106). Nonetheless, in the case of batch #103 after 45 days at the two experimental temperatures, it has evolved to a three-modal distribution type, whereas for batches #102 and 106, they have remained in a pseudo-modal distribution in all the cases (Figs. 9 and 10). This effect is related to emulsion stability, since batch #103 resulted to be the more unstable emulsion in shear viscosity. Also, viscoelasticity seems to be affected by the three-modal distribution, where a particle network formation (terminal behaviour) was more evident for batch #103.

The rheological data demonstrates that it is possible to use caseinate batch #102 to prepare the alcohol-emulsion containing 4 wt% of protein without immediate flocculation. Inevitably, even at a slower flocculation rates, the formation of a particle network

does eventually occur, and consequently a stabilization enhancement of the emulsion during extended storage can be seen at a rather similar rate, depending on protein concentration [25,26]. At higher protein concentrations, the flocculation driving force is even stronger [12,27,28] and the addition of alcohol has significantly less influence than the protein and the ion content in the emulsion.

Moreover, regarding viscosity, mixtures of 20/80 and 40/60 (i.e., batches #102 and #106, in Fig. 6) with calcium caseinate were more stable than the 80/20 samples, presenting more stable viscosity values in all cases. This is an advantage for the elaboration of liqueur creams because it can stabilize formed micelles and avoid the possible aggregation or precipitate formation (i.e. flocculation/coagulation and coalescence). Essentially, a smaller mean particle diameter influences the stability and the properties of emulsions because as long as the particle size of the dispersed droplets is smaller, the system is more stable and visually the emulsion is more transparent [2,8,11,12,20,27,29].

Finally, images from optic microscopy analysis of the batches of caseinate investigated are shown in Fig. 11. The microphotographs show the forming of a network due to the size of the formed micelles and avoiding the possible aggregation or precipitate. Since, the figure shows that independently of the kind of caseinate employed in the emulsions, all blends are heterogeneous, exhibiting a more unstable (i.e. flocculation and coalescence) network in the batch #103 (dark area, Fig. 11a).

The microphotographs presented a macromolecular dispersion that became less agglomerated in the batches #102 and #106 (Fig. 11b and c) than #103 batch. On the other hand, the change in the aggregation state of the different types of caseinate can be explained by considering that the lower droplet size causes a reduction of the free energy associated to the strength of the depletion-interaction and the creation of a larger specific surface area in the fine emulsion and this will simultaneously be accompanied by a reduction in the amount of unabsorbed protein, possibly existing as caseinate submicelles as described by Dickinson and co-workers [11,27]. The size of the formed micelles and the possible aggregation or precipitate formation-swelled increased with the storage time, the emulsion presented a completely different structural organization in the batch #103 (Fig. 11).

From the microphotographs it was evident that the emulsion containing batch #103 was the more unstable, and that the emulsions containing batches #106 and #102 formed a stable network. The micrographs presented aggregates with a size dependent on total ion concentration. The structure may also be responsible for the stability of the caseinate in the emulsion.

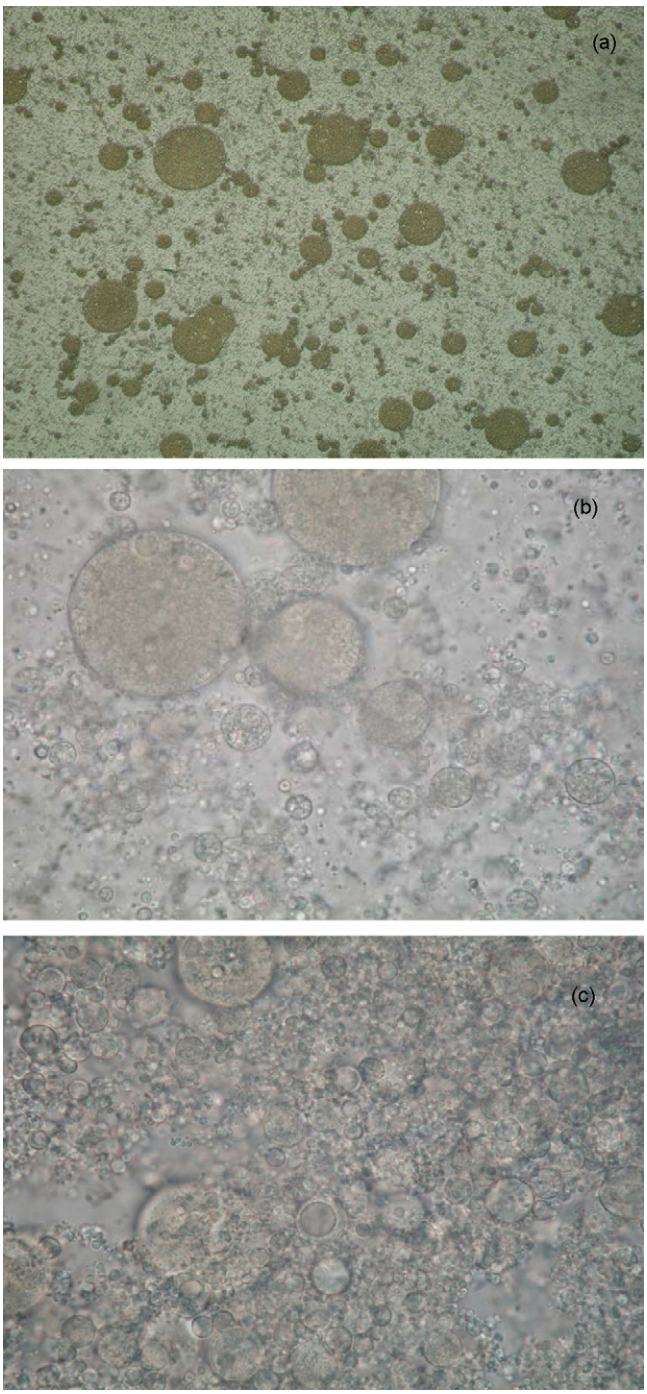

Fig. 11. Pictures with different type of caseinates: (a) Batch #103, (b) Batch #102, and (c) Batch #106.

4. Conclusions

The influence of alcohol on the stability and rheology of emulsions containing excess of unabsorbed sodium caseinate has been examined. The prepared emulsions follow a non-Newtonian behaviour (i.e., $n < 1$). The emulsions viscosity values increased with storage time, being also dependent on temperature. Furthermore, the volumetric diameter $d(4,3)$ showed a dependence on the storage time and coalescence of emulsions was observed in all cases to be dependent on the alcohol content. This effect was associated to the ionic content in the different caseinate batches. Significant changes in viscosity and particle size distribution were observed in caseinate batch #103, which showed higher Na^+ ions content in combination with the Ca^{++} ions. Nevertheless, minor changes were found in samples prepared with caseinate batch #102, which has the lowest total ion content. Thus the higher stability of this type of alcoholic emulsions is probably associated to their ionic content. At the beginning the emulsion prepared with caseinate batch #102 was more stable displaying a one-modal distribution of particle size. This is due to the minor total ion content and to the structure that the emulsion adopts.

Caseinate mixtures 40/60 (i.e., batches #102 and 106) were more stable, presenting intermediate viscosity values. The viscosity was found to be directly related to the particle size of the emulsions prepared at different casseinate ratios. Emulsions having low viscosity values are an advantage in the elaboration of liqueur creams because formed micelles are more stable, avoiding the possible aggregation or precipitate formation. Although a small initial average droplet size in prolonged storage times does produce a short-term stability improvement, even though there is not yet a significant effect on long-term product stability. Finally, the results

on microscopy suggest that the final structure plays an important role in the stability of the alcoholic emulsion with industrial interest in food emulsions, particularly in the elaboration of cream liqueurs.

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