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Rheological analysis of highly concentrated w/o emulsions

Received: 20 February 1997
Accepted: 20 January 1998

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Abstract A series of highly concentrated lipophilic cosmetic emulsions were analysed, in order to determine their rheological and textural properties, as a function of their microstructure. The originality of this study lies in the methodology used, especially the shear-stress scanning analysis. The results of a very powerful and comprehensive dynamic rheological analysis suggest the existence of two critical volume fraction values: besides the “close-packed” value ϕ_c , a “slack-packed” value ϕ_0 , close to 0.60 could be demonstrated. It has been shown that the close-packed structure is stable under shear; in contrast, the slack-packed configuration, defined as $\phi_0 < \phi < \phi_c$ is unstable under shear. A comparison with the-

oretical models, especially that of Princen, showed good agreement and allowed the close-packed value ϕ_c to be defined more precisely as 0.67. The gap between 0.67 and 0.74 is probably indicative of a highly polydisperse distribution, as confirmed by microscopic analysis. Flow experiments confirmed the validity of Princen's model.

Key words Emulsion – cosmetics – oscillatory viscoelastic analysis – yield stress – lipophilic emulsions

Introduction

HIPREs (high internal phase ratio emulsions) have already been widely studied both experimentally and theoretically (Barry, 1975; Princen, 1979, 1980, 1982, 1985, 1988; Princen and Kiss, 1986, 1989; Bibette, 1992; Aronson and Petko, 1993; Benali, 1993; Reinelt and Kraynik, 1993; Otsubo et al., 1994). Their viscoelastic properties have been shown to depend on the mean diameter of dispersed particles, polydispersity, interfacial tension and particularly on the dispersed volume fraction. Various authors have suggested the existence of a critical volume fraction beyond which the rheological properties are considerably modified. In fact, beyond this critical fraction, the particles become

organized in a crowded distribution, which gives them the rheological behaviour of a plastic liquid:

- below the yield stress the deformations of the particles are insufficient to allow flow in a global movement and, consequently, elastic behaviour prevails;
- above the yield stress the deformations are sufficient to induce a flow which is characterized by the predominance of viscous effects.

The principal aim of this study was in a viscoelastic analysis of concentrated lipophilic emulsions, which are widely used in the cosmetic industry, with different volume fractions varying over a large interval including the critical volume fraction. Its originality lies in the methodology chosen – *sweeping stress viscoelastic analysis* – which is particularly appropriate for working

on dispersed concentrated emulsion structures and on the transition which they undergo from an elastic to a viscous state. Flow analysis was also used to complete the description of the rheological properties. The results of these analyses were compared with theoretical models found in the literature.

Materials and methods

Materials

Raw materials and composition

The oil phase, which had a density of 0.90 g/cm³ and a viscosity of 5.3 m Pa·s, was hydrocarbons (squalane and cetearyl octanoate) and silicone (cyclic dimethyl polysiloxane). The nonionic lipophilic surfactant used was a sorbitan monooleate (HLB=4.3). The aqueous phase was composed of glycols, hydrated magnesium sulfate, demineralized water and a preservative substance. The basic formulation of HIPREs was as follows (w/w):

Oil phase

Hydrocarbons	4.12
Silicone	5.88
Sorbitan monooleate	4.55

Aqueous phase

Glycols	21.66
MgSO ₄ , 7H ₂ O	5.70
Preservative substance	0.22
Demineralized water	57.87

This formulation was chosen because it constitutes a reference for some products (creams) frequently found in the cosmetic industry.

Method of preparation

HIPREs were prepared at room temperature by incorporation of the oil phase into the aqueous phase with blade stirring at 1900 rpm. After complete addition of the oil phase, the stirring was maintained for 15 min at 3600 rpm. The basic formulation presented a dispersed volume fraction of 85%. Different volume fractions of w/o concentrated emulsions were obtained by dilution with the oil phase. Knowing the density of this phase, different volume fractions were calculated from the relationship:

$$\Phi = \frac{m_{\text{water}}/\rho_{\text{water}}}{m_{\text{water}}/\rho_{\text{water}} + m_{\text{oil,phase}}/\rho_{\text{oil,phase}}}$$

with m : either water or oil phase mass ρ : either water or oil phase density.

Seven formulations with volume fraction of 60, 65, 70, 73, 74, 75 and 80% (with a possible error in ϕ values of approximatively 1%) were prepared.

Methods

In order to characterize the different concentrated lipophilic emulsions, optical, electronic microscopy and rheological analyses were performed.

Microscopy

Optical microscopy

These observations were carried out on diluted or initial samples with an optical microscope (OLYMPUS) equipped with a camera, at a magnification of $\times 125$.

Freeze-fracture electron microscopy

This analysis allowed the granulometry and the size distribution of the different samples to be visualized. The samples were frozen in propane cooled with liquid nitrogen (-196°C) and split with a knife blade. After shadowing the fractured surfaces with platinum, the samples were dissolved and the washed replicas were examined under a transmission electron microscope.

Rheological analysis

The rheological behaviour of these different emulsions was studied at $20^\circ\text{C} \pm 1^\circ\text{C}$ with a controlled stress rheometer HAAKE RS 100 (RHEO, Champlan, France). The shear geometry was performed with a cone plate geometry using a 2 cm diameter and a cone angle of 4° . Different rheological measurements were carried out:

Oscillatory viscoelastic analysis

During the assay, the sample was submitted to a harmonic shear in which the stress $\tau(t)$ and the strain $\gamma(t)$ were varied sinusoidally with a pulsation ω . The shear stress $\tau(t)$ and the shear strain $\gamma(t)$ are respectively defined by:

$$\tau(t) = \tau_0 \cos \omega t \quad \gamma(t) = \gamma_0 \cos(\omega t - \delta)$$

The evolution of the dynamic parameters as a function of the maximal amplitude of the stress τ_0 was supplied by shear-stress sweeping. All measurements were carried out at a frequency of 1 Hz. Some analyses were also performed at other frequencies in the range 10^{-2} Hz–1 Hz. The main rheological parameters used for this study were:

- G^* , the shear modulus (or complex modulus), $G^* = \frac{\tau_0}{\gamma_0}$
- δ , the phase angle of the stress with respect to the strain,

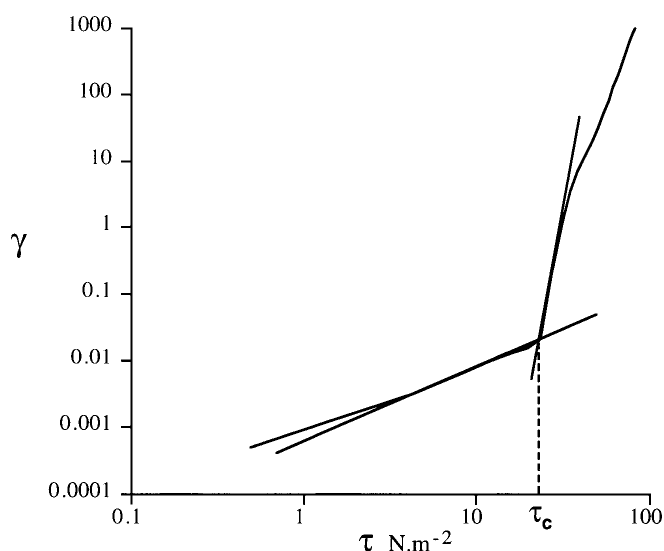


Fig. 1 Determination of τ_c from $\gamma=f(\tau)$ after a steady state analysis for emulsion with a volume fraction ϕ of 75%

- G'' , the loss modulus, $G''=G^* \sin \delta$,
- $(\tau_0)_c$, the critical stress at which G'' reaches a maximum.

Steady state analysis

This test consisted in submitting a sample to an instantaneous stress τ which remained constant during a time t (waiting time chosen in order to reach the steady state). Simultaneously, the evolution of the corresponding shear strain γ was recorded and the values of γ were measured at the end of the test. The yield values were determined by plotting the deformation versus shear stress using a double logarithmic scale to cover a wide shear stress range: the graph $\gamma=f(\tau)$ (Fig. 1) shows two regions which represent firstly the elastic linear regime and secondly the viscous regime. The intersection of the two segments gives the yield value τ_c . Furthermore, beyond τ_c , the values of the shear rate $\dot{\gamma}$ can be measured and the rheograms $\tau=f(\dot{\gamma})$ recorded.

The different rheological measurements were carried out three times. All experiments were reproducible with C.V.<5%.

Results and discussion

Microscopic observation of concentrated emulsions

The optical and freeze-fracture electron microscopy analyses showed that all the systems studied were polydisperse with a droplet size between 0.1 and 10 μm . The electron micrographs (photo 1), taken on undiluted emulsions with a high volume fraction ($\phi=85\%$) revealed a compact network with a very large polydisper-

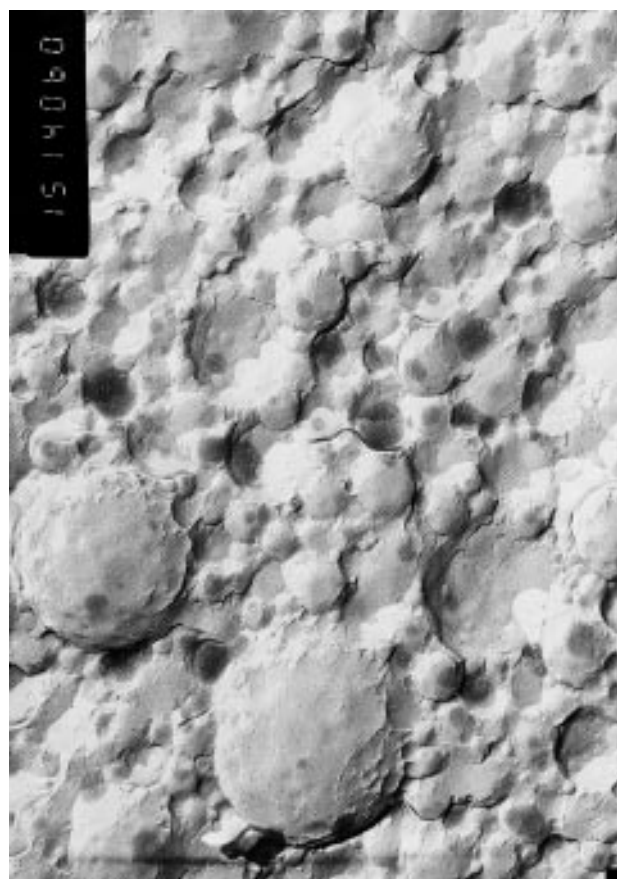


Photo 1 Freeze-fracture micrograph depicting the basic formulation which a maximal volume fraction of $\phi=85\%$ (45 000 \times magnification)

sity of the droplet sizes. Although no specific granulometric analysis was performed, the observations on the electron micrographs suggest that the mean droplet radius (Sauter radius, for instance) could be close to 1 μm .

Influence of the volume fraction on the rheological characteristics of concentrated lipophilic emulsions

Although other studies in which dynamic measurements have been made can be found in the literature (Ebert et al., 1988; Pons et al., 1993), no sweep-stress analysis has been performed until now. The originality of this study lies in the use of sweep-stress dynamic measurements to establish the influence of the volume fraction on the rheological properties. Oscillatory analyses were carried out on lipophilic emulsions with different volume fractions (ϕ). During a shear-stress scan, the basic viscoelastic parameters such as shear modulus G^* , phase angle δ and loss modulus G'' were recorded for variable values (increasing or decreasing) of the stress amplitude τ_0 .

Increasing curves

Figures 2a and b show the evolution of G^* and δ according to the increase of shear stress τ_0 (Up curve). At low shear stresses, a zone of constant response (plateau region) indicating an unaltered structure, not disturbed by shear, was observed. In this linear region, the applied strains were very low; the particles were crowded and could not move freely past one another: this defines the *elastic domain*. In this low strain region, a quantitative analysis of G^* and δ was valid and consequently carried out. At higher shear stresses, a decrease of G^* and an increase of δ were observed, the applied strain being sufficient to allow the particles to move past one another and inducing a transition to the *viscous domain*: the emulsions then become more viscous than elastic. Only a qualitative analysis of the basis vis-

coelastic parameters could be envisaged in this large strain region. This change from the elastic to the viscous domain can be defined precisely by noting the stress (or the strain) when G'' reaches a maximum (Fig. 2c), this critical stress (τ_0)_c being considered as a yield stress. The G'' peak confirms and elucidates the transition from the elastic to viscous region.

– From an empirical point of view, the existence of a G'' maximum means a transition phenomenon in most cases, whatever its nature.

– From a microstructural point of view, this peak probably means that the dissipation energy is maximal when the droplets are deformed and flattened enough to allow flow despite the crowding.

Whatever the volume fraction studied, a plateau zone appears, at least for the G^* values (Fig. 2a): short for $\phi < 70\%$, it becomes extended for higher volume frac-

Fig. 2a Shear modulus G^* vs. stress for emulsions with different volume fractions

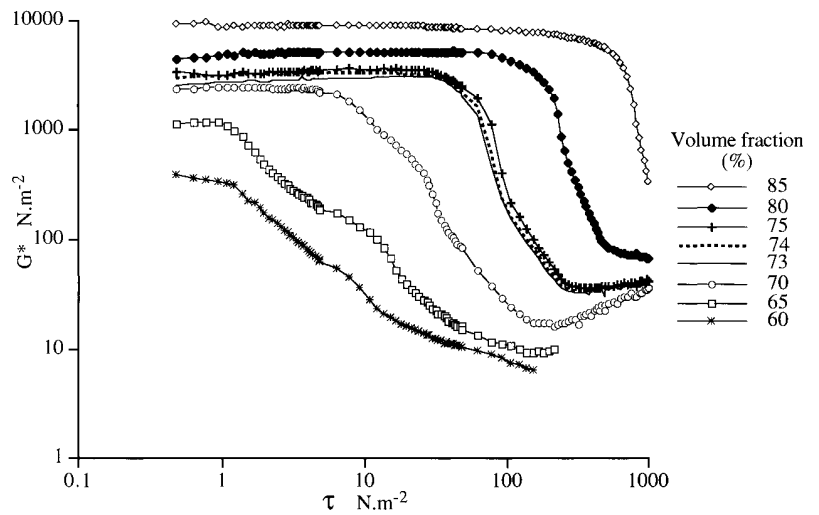
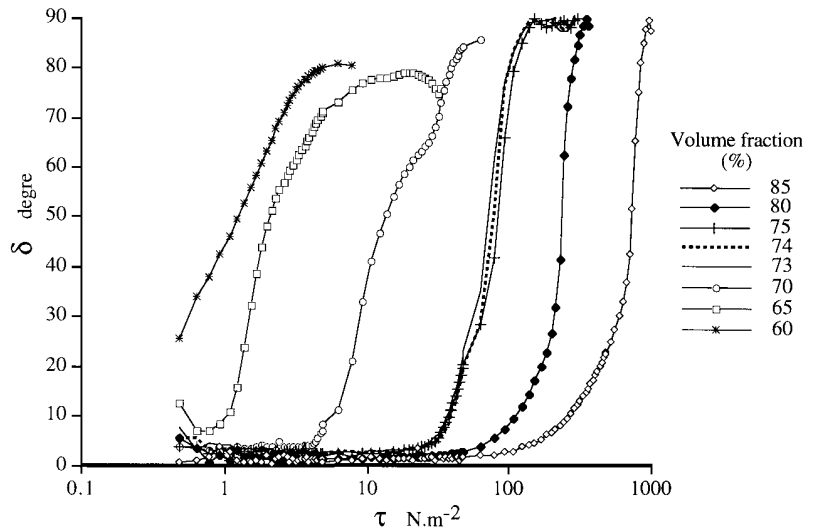


Fig. 2b Phase angle δ vs. stress for emulsions with different volume fractions



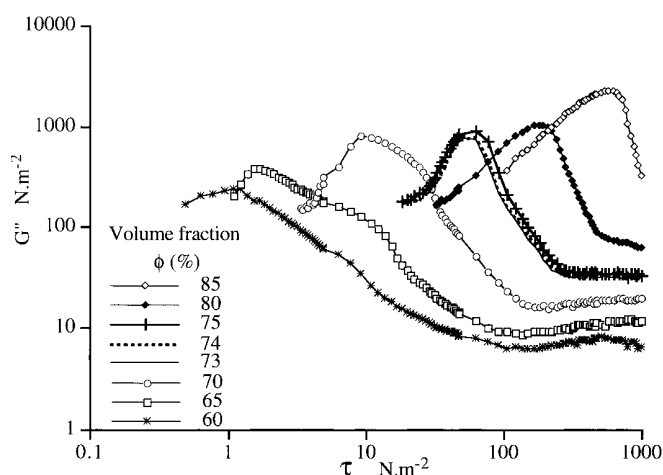


Fig. 2c Loss modulus G'' vs. stress for different volume fractions

tions. Moreover, the recording of the main viscoelastic parameters (G^* , δ) (Table 1) in the linear region shows a decrease of G^* and an increase of δ when the volume fraction decreases. This indicates the loss of the elastic character of these systems resulting from a structural modification of particles to a less and less compact network. Similarly, the more or less marked character of the transition from the elastic to the viscous domain largely depends on the volume fraction. It is more pronounced when ϕ increases. Moreover, the stress that has to be applied to allow the particles to flow (yield stress) is larger when the system becomes more compact and ϕ is higher (Table 2). From these results, it appears that the decrease of the volume fraction is accompanied by a decrease of elasticity, expressed by the values of G^* and δ , which are the reflection of a less and less compact organization, especially when $\phi < 70\%$. Indeed, although they display qualitatively similar behaviour to the emulsions with a volume fraction $\phi > 70\%$ (plateau zone, yield stress), the emulsions with a volume fraction between 60 and 70%

show significant quantitative differences in behaviour, since G^* , δ and $(\tau_0)_c$ evolve rapidly with the volume fraction (particularly in the case of 70–65%). These observations can be explained by assuming that two critical fraction values exist:

- a critical fraction value ϕ_c of close packed organization in which the droplets are in contact with each other: this ϕ_c volume fraction will be called the “close-packed” value. The corresponding behaviour is a purely elastic one with very low δ values.

This purely elastic behaviour was verified at other frequencies in the range of 10^{-2} Hz to 1 Hz, within the margin of experimental error.

For a monodisperse emulsion, the minimal value of ϕ_c is 0.7405. For typical polydisperse systems, the literature refers to a close-packed value different than 0.7405 and smaller, in the case of a non multimodal distribution, Princen (1988). The δ -values in Table 1 suggest that a quasi-ideal elastic behaviour appears from a value intermediate between 0.65 and 0.70. The existence of critical volume fraction ϕ_c somewhat lower than 74% (down to 65%) is in accordance with several theoretical and experimental studies on concentrated dispersions (Otsubo and Prud’Homme, 1994; Werff and Kruif, 1989, Quemada, 1989). This ϕ_c value will be more precisely defined by correlation with theoretical models.

- Besides the lower ϕ_c , another critical volume fraction ϕ_0 might exist, above which layers of close-packed spheres can no longer freely slip past one another: this ϕ_0 volume fraction will be called “slack-packed” value. For a monodisperse emulsion, ϕ_0 was found theoretically to be 0.6046, (Princen and Kiss, 1986). For $\phi_0 < \phi < \phi_c$, a plastic behaviour, but with very low yield stress values and relatively high δ -values, meaning a slacker organization than in the close-packed one, is expected. Tables 1 and 2 suggest that the ϕ_0 value is certainly close to 0.60, possibly a little lower. In any case, this value is higher than 0.55, as confirmed by tests which showed a liquid behaviour for this concentration.

Table 1 Mean values of G^* and δ in the plateau region for various volume fractions of emulsions

ϕ (%)	85	80	75	74	73	70	65	60
G^* (N/m ²)	8800	5000	3300	3200	2800	2500	900	400
δ (°)	1	1	2	3	3	4	14	32

Table 2 Yield stress values

ϕ (%)	85	80	75	74	73	70	65	60
$(\tau_0)_c$ (N/m ²)	592	183	63	63	48	9	1	1

Decreasing curves

By subjecting a sample to an increase (up) and a decrease (down) shear stress, it is possible to determine whether the modifications of structure are reversible or not.

During an up-down scanning shear stress, the up and down curves were practically superposed for $73\% < \phi < 85\%$ (Fig. 3a), reflecting an unaltered structure which was not disturbed by the shear. On the other hand, when $70\% < \phi < 73\%$ (Fig. 3b), the curves were no longer superposed at the plateau region. Below 70%, the return curves did not have a linear zone. Consequently, it seems that the shear did not alter the structure of emulsions when they presented a compact network organization. The photos obtained with an optical microscope from sheared (10^3 s^{-1}) or unsheared sam-

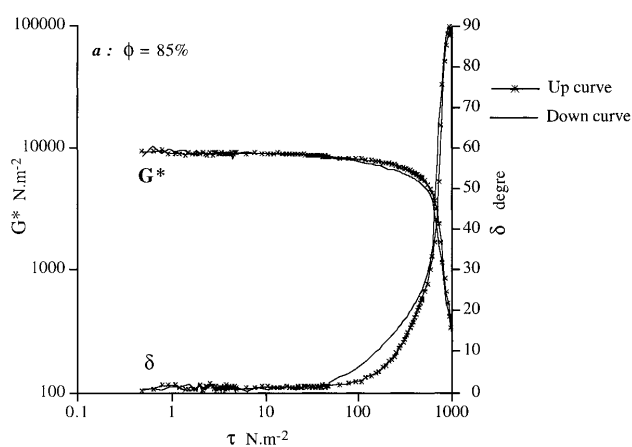


Fig. 3a Evolution of G^* , δ , during increasing shear (—) and decreasing shear scanning (---) for emulsions with a high volume fraction ($\phi=85\%$)

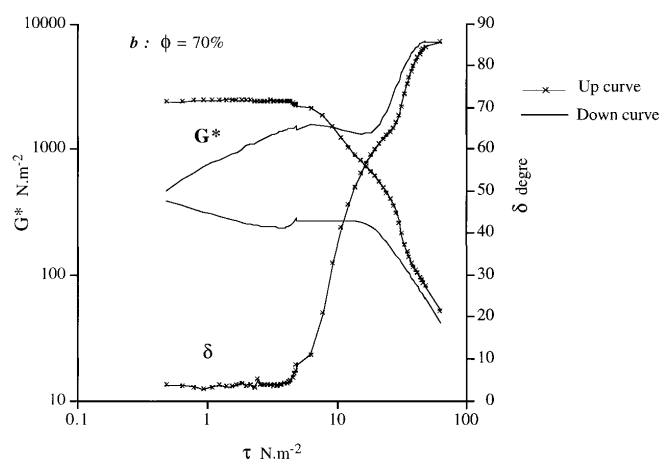


Fig. 3b Evolution of G^* , δ , during increasing shear (—) and decreasing shear scanning (---) for emulsions with a low volume fraction ($\phi=70\%$)

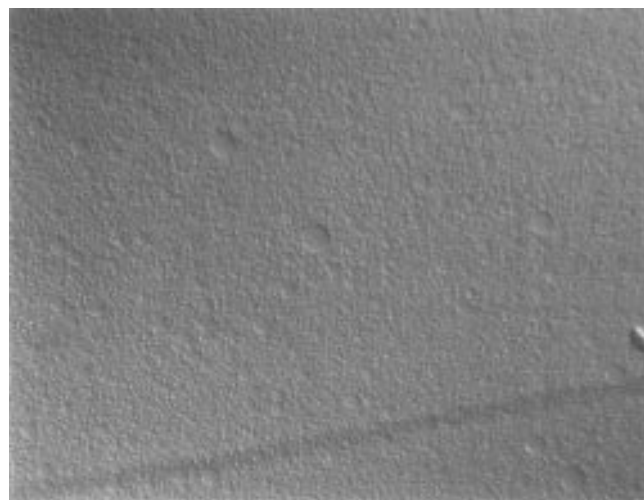


Photo 2 Representation of concentrated emulsion with a low volume fraction $\phi=60\%$ before shear ($100\times$ magnification)

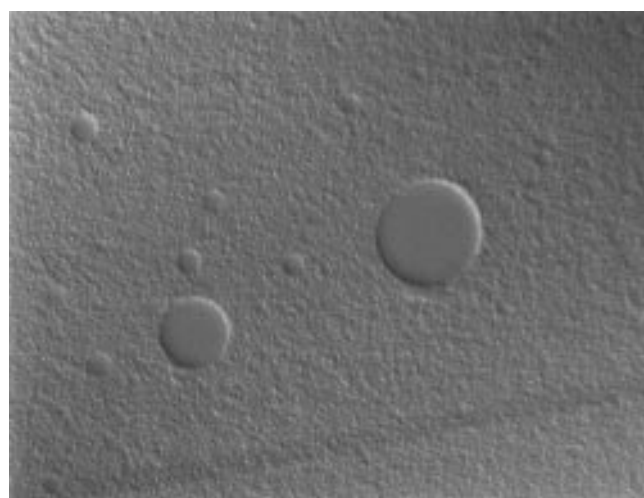


Photo 3 Representation of concentrated emulsion with a low volume fraction $\phi=60\%$ after shear (10^3 s^{-1}) ($100\times$ magnification)

ples confirm that for high ϕ , the shear did not alter the globule size. On the other hand, for more diluted volume fractions $70\% > \phi > 60\%$, when the organization of the particles became slack, the photos (2–3) testify to an increase in the size, but also to an increase of the droplet polydispersity.

This appearance of a multimodal size distribution could be explained either by coalescence or by modifications induced in the low volume fraction by the shear effect. These results emphasize the very valuable and powerful character of dynamic rheological analyses in the characterization of complex structures such as the HIPREs; they provide a much more comprehensive description than steady-state flow experiments, since they take into account both viscous and elastic properties.

Fig. 4 $\tau=f(\dot{\gamma})$ for emulsions with different volume fractions

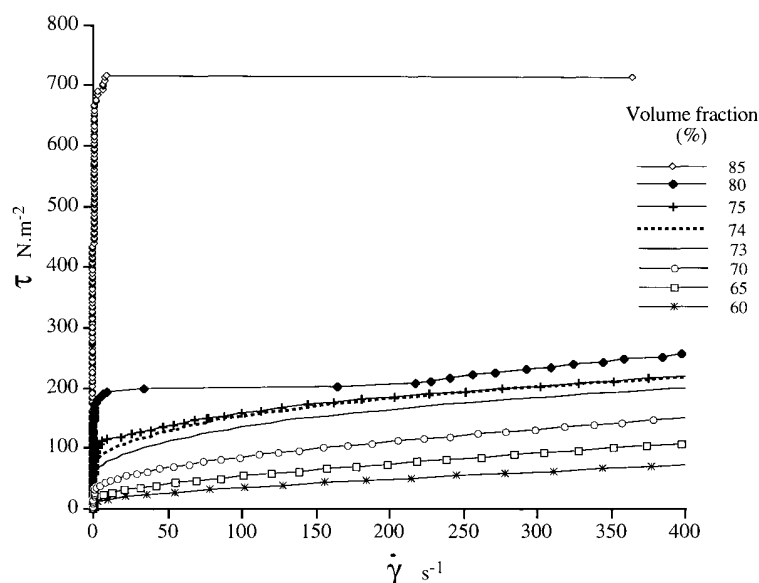


Table 3 Determination of the adjustment parameters (τ_c , n) for the different emulsions

ϕ (%)	85	80	75	74	73	70	65	60
τ_c (N/m ²)	450	180	82	65	60	25	11	5
n	–	–	0.54	0.51	0.56	0.53	0.60	0.50
σ (%)	–	–	20	10	10	6	4	4

Steady-state and dynamic analyses were carried out at the same time. The results (Fig. 4) show that all the emulsions presented a *plastic liquid behaviour*. The best-fit model of the experimental results is the Herschel-Bulkley model defined by:

$$\tau = \tau_c + K\dot{\gamma}^n$$

where τ_c is the yield stress.

For emulsions whose volume fraction was between 60% and 75% (Table 3), a good theoretical/experimental correlation ($C.V.<20\%$) was observed and it could be established that the exponent n was close to 0.5. On the other hand, for $\phi>75$, it was not possible to obtain a good fit for the flow curves, because of the lack of points: when the emulsions were organized in a compact network, the stress necessary to allow the particle flow was so high that when it was attained, flow suddenly appeared and produced an excess of speed almost instantaneously. The Herschel-Bulkley fit provided a yield value τ_c . Another τ_c determination was obtained by recording of the graph $\dot{\gamma}=f(\tau)$. It is interesting to compare the three yield values obtained by dynamic and steady-state analysis. There is a good correlation between these different methods (Fig. 5). Although the yield values are not exactly the same, they are rela-

tively close and, in any case, they are of the same order of magnitude. It is worth emphasizing that the three methods give complete agreement about the plastic behaviour, and confirm the existence of a yield for $\phi\geq 60\%$.

Correlation with the theoretical models described in the literature

Different theoretical models of the rheological properties of concentrated emulsions have been put forward over the last few years (Princen, 1982; Khan and Armstrong, 1986; Werff and Kruif, 1989; Quemada, 1985). A very complete model was proposed by Princen (1979, 1980, 1982, 1985, 1988), Princen and Kiss (1986, 1989). For a two dimensional model of a monodisperse highly concentrated emulsion, by assuming that the dispersed droplets are arranged in a hexagonally close-packed configuration, Princen was able to derive the exact stress vs. strain or strain rate relationships, in both the elastic and flow regions. By simple analogy and dimensional analyses, Princen extended the prediction to real polydisperse emulsion. The theoretical model can be summarized by the following relationships:

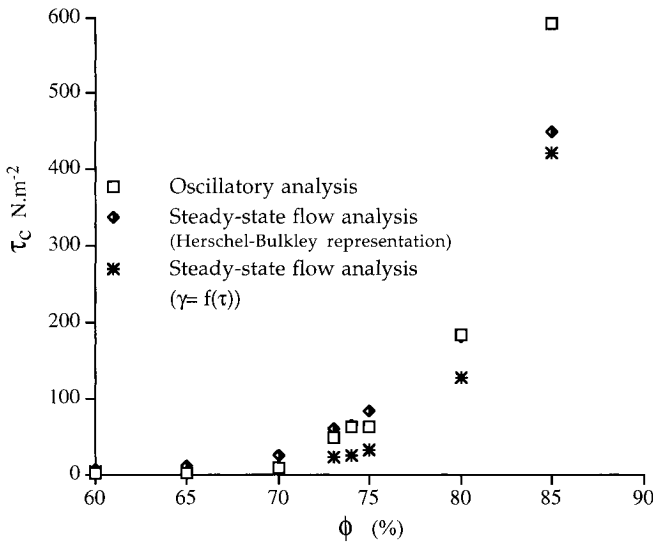


Fig. 5 Comparison of τ_c values established by different methods as a function of volume fraction

– shear modulus:

$$\tau < \tau_c \text{ (elastic region)} \quad G^* = A \frac{\sigma}{R_{32}} \phi^{1/3} (\phi - \phi_c) \quad (1)$$

– τ - $\dot{\gamma}$ relationship:

$$\tau > \tau_c \text{ (flow region)} \quad \tau = \tau_c + K \dot{\gamma}^{1/2} \quad (2)$$

where σ : interfacial tension, ϕ_c : critical volume fraction, R_{32} : Sauter radius (volume-surface) of the undeformed drop, A : fit constant; which are supposed to be valid for $\phi > \phi_c$ (close-packed value). Recently, this model has been examined critically by Mason et al. (1995) who have found that G^* evolves as $\phi(\phi - \phi_c)$.

Correlation for the elastic region

In order to determine the Princen critical volume fraction ϕ_c , linear regression analysis of the graph $\frac{G^*}{\phi^{1/3}}$ vs. ϕ was performed, when ϕ varies from 0.73 to 0.85 (Fig. 6).

This interval was chosen:

1) so that the ϕ -values were unequivocally above the presumed close-packed value. Therefore $\phi = 0.60$ and $\phi = 0.65$ were excluded.

2) In order to avoid gravitational syneresis, if the dilution is too high, there might appear a vertical gradient in ϕ which could result in an overestimate of the measured G^* (Princen and Kiss, 1986). So the value $\phi = 0.70$, which indeed seemed to give overestimated G^* values, was excluded. However, it does not seem reasonable to exclude the values up to $\phi = 0.75$: indeed, the dispersed and continuous phases present relatively close density values so the drainage is probably hindered down to 0.73. As a matter of fact, none of our

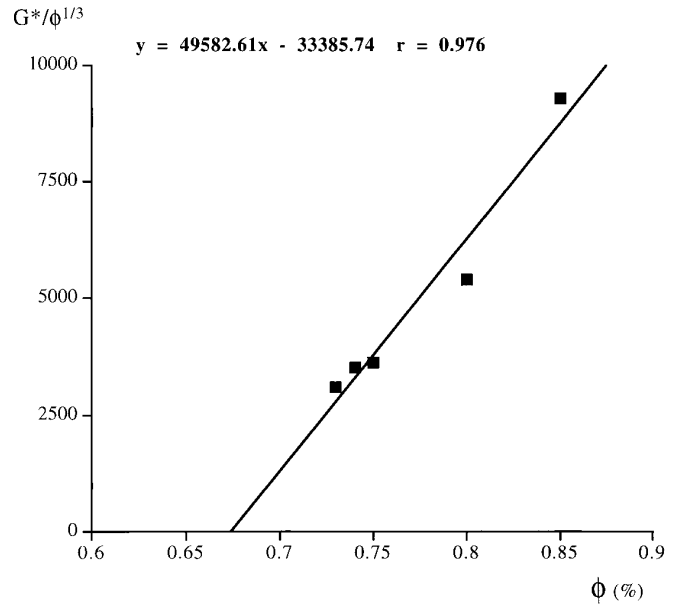


Fig. 6 Evolution of $\frac{G^*}{\phi^{1/3}}$ vs. ϕ between 0.73 and 0.85

emulsions with $\phi \geq 0.73$ showed any sign of drainage. Moreover, if the values up to 0.75 were excluded, the analysis would lead to $\phi_c = 0.73$, which is appreciably higher than the presumed close-packed value which was previously found to be about 0.65.

Linear regression analysis provides a value of $\phi_c = 0.67$, which is very close to the presumed value. Linear regression analysis of the graph $\frac{G^*}{\phi}$ did not lead to a very different value (0.66). Whatever the ϕ_c value retained (0.66 or 0.67), they are relatively low with respect to the theoretical value (0.74) or even compared with the Princen value (0.712). It is possible that it was underestimated by the linear regression. However, this ϕ_c value is possible, taking into account the very poly-disperse but unimodal character of emulsions (Princen and Kiss, 1986, 1989). It is worthwhile recalling that some estimations of the ϕ_c value in the literature are even lower and very close to ϕ_0 , (Otsubo and Prud'Homme, 1994; Quemada, 1985). In the absence of a value for the R_{32} Sauter radius, it was impossible to compare the theoretical and experimental G^* -values. However, it is interesting to deduce the value of R_{32} from the theoretical values of the shear modulus by assuming the validity of Eq. (1): taking $A = 1.77$ (Princen value) $\phi_c = 0.67$ and $\sigma = 3$ mN/m (experimental value determined by interfacial tension analysis (Fig. 7)), it was found that the Sauter radius R_{32} would be between 1 and 2 μm . This value seems reasonable, at least in order of magnitude.

Furthermore, it should be noted that the elastic shear modulus, G , defined by Princen in his model, is a static parameter determined during creep measurements. G

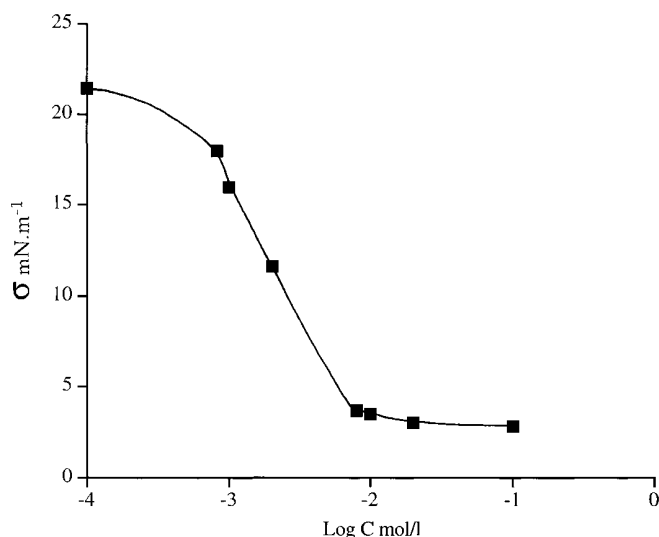


Fig. 7 Interfacial tension as a function of the concentration of lipophilic surfactant

was established in a linear small-strain regime. In the present work, the dynamic complex modulus G^* is used in Princen's equation. Creep measurements made on our w/o systems allowed us to check that the dynamic shear modulus had the same value ($\pm 10\%$) as the static shear modulus. These results are not surprising because it had already been shown that G^* values in the linear regime were almost independent of the frequency, at least at relatively low frequencies [10^{-2} Hz–1 Hz].

Correlation for the flow region

In agreement with theoretical predictions, beyond ϕ_c the flow experiment displayed a plastic character and a shear thinning behaviour when the yield stress is exceeded. The best fit of the plastic rheograms is provided by a Herschel-Bulkley model (2) with $n \approx 0.5$ as expected from the theory (Table 3). It is interesting to emphasize that the agreement was found to be good even for $\phi = 0.60$ and $\phi = 0.65$. So the validity of Eq. (2) could be extended, below ϕ_c , up to ϕ_0 .

In conclusion, the agreement between the experimental rheological results and Princen's model is good; it is even surprisingly good if we consider that Princen's exact prediction concerned mainly a monodisperse emulsion and not a highly polydisperse distribution as in the present work. It seems that the use of the Sauter radius

allows a very high polydispersity to be taken into account reasonably. The use of dynamic shear modulus in Princen's model results in a good correlation which demonstrates that this approach by sweeping stress viscoelastic measurements is a valid and novel one.

Conclusion

Concentrated lipophilic emulsions, as frequently used in cosmetic applications, containing different volume fractions, have been subjected to a full rheological characterization, in particular a very powerful oscillatory viscoelastic analyses by stress scanning, and also steady-state flow analyses. These analyses have allowed us to establish very useful methods of evaluating concentrated emulsion systems in the cosmetic industry. It has been demonstrated that a decrease of the volume fraction is accompanied by a decrease of the elastic character (plateau less and less well defined), meaning a more and more slack network organization of particles. Similarly, the transition from the elastic domain to the viscous domain depends closely on the volume fraction with a more marked character when ϕ becomes higher. This behaviour suggests that two critical volume fraction values can appear in a sweep stress oscillatory test: besides the "close-packed" value ϕ_c , there could exist a "slack-packed" value ϕ_0 , whose the value is very close to 0.60. It has been shown that the close-packed structure is stable under shear; in contrast, the slack-packed configuration, defined for $\phi_0 < \phi < \phi_c$ is unstable by shear.

Our results have been successfully compared with the Princen model, establishing a critical volume fraction ϕ_c close to 0.67. It is significantly lower than the monodisperse (0.74) or Princen values (0.71). This value probably means the existence of a very large, but not multimodal size, distribution. Steady-state flow experiment confirmed the validity of the theory: it was found that the best fit of the rheograms was provided by a Herschel-Bulkley model, with an exponent value very close to 0.5. In fact, no improvement of Princen's model is suggested by our data. The originality of this study lies in the methodology used, especially shear-stress scanning analysis.

Acknowledgments We thank T. Pouget for his large contribution to freeze-fracture electron microscopic analysis. We thank the French Ministry of Industry for partial support (assent 94292620).

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