

Viscoelasticity of Water / Isopropanol / Alkyd resin emulsions

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Abstract

The aim of the study is to assess the role of the water droplets on the viscoelastic properties of water + isopropanol / alkyd resin emulsions and to confirm if dynamic rheometry on a large frequency scale can provide a good tool for the characterization of interfacial properties.

Introduction

The introduction of water droplets in the ink matrix during the lithographic process produces drastic modifications of the rheological behaviour of the ink. In the literature, the flow properties of the lithographic emulsions have been studied by Bassemir (1987) and Durand (1992). The concept of fracture shear stress for an emulsion (the maximum shear stress before emulsion breaking) is used in this context.

The viscoelasticity of printing inks was investigated in the past by Oittinen (1976, 1992) and Rohn (1987). This behavior is of paramount importance for the transfer properties on the press, and indeed the initiation of ink splitting in the nip is described by Aspler (1993) as a viscoelastic process.

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The water dispersed in the ink enhances the viscoelastic properties of the latter. Interesting studies have been made in the field of dynamic rheometry by Barry (1975), Komatsu (1977), Eshuis (1984), Mellema (1987) and Orecchioni (1984), in order to understand the viscoelastic behavior of emulsions of two non-miscible fluids.

We have studied various emulsions with dynamic rheometers, on a large frequency range (0.1 to 250 Hz) at room temperature and observed that the water inclusions enhance the elasticity of the emulsions at low frequency. This increase of the elastic contribution in the flow domain is accompanied by a long relaxation time process which affects the elastic modulus G' . Mellema (1987), Orecchioni (1984), Palierne (1990), Graebing (1993) and Scholz (1989) showed that this rheological behavior depends on the physical properties like the radius of the inclusions, the interfacial tension and the zero-shear viscosity of the two phases.

Palierne (1990) develops a theoretical model which describes the linear viscoelastic behavior of two-phase polymer blends in the melt which was adapted to our water + isopropanol / alkyd resin systems. The resulting correlations were compared with the experimental results. Such comparisons give us some meaningful information about the interfacial properties (interfacial tension, distribution of the isopropanol molecules at the interface) if the average radius of the droplets is known.

1. Dynamic rheometry

The rheological behavior of printing inks, or more generally of polymers in the melt, is a combination between elastic and viscous contributions which depends on the molecular weight and the structure of the different components and the temperature of the sample.

There are different ways to measure the elastic / viscous ratio of a sample, essential creep tests or oscillating tests. We measured the classical viscoelastic parameters with oscillating experiments.

The sample is sheared in a sinusoidal deformation:

$$\gamma = \gamma_0 \cdot \sin(\omega t) \quad (1)$$

The amplitude of the deformation must be small in order to remain in the linear viscoelasticity range. The phase of the resulting stress σ is shifted by an angle δ so that:

$$\sigma = \sigma_0 \cdot \sin(\omega t + \delta) \quad (2)$$

δ lies between 0 and 90 ° for a viscoelastic material. The complex mathematical notation gives:

$$\begin{aligned} \gamma^* &= \gamma_0 \cdot e^{i\omega t} \\ \sigma^* &= \sigma_0 \cdot e^{i(\omega t + \delta)} \end{aligned} \quad (3)$$

The complex relaxation modulus is defined as :

$$G^* = \frac{\sigma^*}{\gamma} = G' + i \cdot G'' \quad (4)$$

$$\text{where } G' = \frac{\sigma_0}{\gamma_0} \cdot \cos \delta \quad \text{and} \quad G'' = \frac{\sigma_0}{\gamma_0} \cdot \sin \delta \quad (5)$$

G' is the storage modulus (elastic part) and G'' is the loss modulus (viscous part). The factor $\tan \delta$ which is the ratio of the loss modulus and the storage modulus

$$\tan \delta = \frac{G''}{G'} \quad (6)$$

is of paramount importance to define viscoelastic properties.

2. Model for rheological behavior of an emulsion of 2 incompressible fluids

Palierne (1990) simulated the viscoelastic behaviour of an emulsion of 2 incompressible fluids to which an interfacial agent is added. He took into account the general fact that the interfacial tension depends on the shear deformation and the variation of the interfacial area. The mechanical interactions between inclusions were treated by a method similar to that of the Lorentz spheres in electricity.

If the interfacial tension is independent of the variation of the interfacial area and of the local shear, the resulting complex shear modulus of the emulsion is obtained as a function of the morphology and dynamic properties of the emulsion (volume fraction of the inclusions, interfacial tension, size distribution of the droplets, complex shear modulus of the 2 phases):

$$G^*(\omega) = G_m^*(\omega) \frac{1 + 3 \sum_i \phi_i H_i(\omega)}{1 - 2 \sum_i \phi_i H_i(\omega)} \quad (7)$$

$$H_i(\omega) = \frac{\frac{4\gamma}{R_i} (2G_m^*(\omega) + 5G_i^*(\omega)) + (G_i^*(\omega) - G_m^*(\omega)) (16G_m^*(\omega) + 19G_i^*(\omega))}{\frac{40\gamma}{R_i} (G_m^*(\omega) + G_i^*(\omega)) + (2G_i^*(\omega) + 3G_m^*(\omega)) (16G_m^*(\omega) + 19G_i^*(\omega))} \quad (8)$$

with,

$G^*(\omega)$	the complex modulus of the emulsion
$G_i^*(\omega)$	the complex modulus of the dispersed phase
$G_m^*(\omega)$	the complex modulus of the matrix
R_i	the radius of the droplets
ϕ_i	the volume fraction of the inclusions of radius R_i
γ	the interfacial tension.

Graebing and Palieme (1993) found a very good correlation between the theoretical predictions and the experimental results obtained with different emulsions of 2 polymers and showed that viscoelastic measurements could be used to estimate the interfacial tension directly in the emulsion if the size of the droplets was known.

In the foregoing study, we tested this method on water + isopropanol / alkyd resin emulsions in order to know if it could give us some meaningful results about the morphology of the emulsions.

3. Experimental conditions and results

Material

- distilled water containing 15 % isopropanol was used as the disperse phase.
- an alkyd resin (LV 807, Sun Chemical) constituted the matrix ($\eta_0 = 115 \text{ Pa.s}$ at $21 \text{ }^\circ\text{C}$).

Preparation of the emulsions

A Dispermat CV was used to disperse the aqueous solution in the alkyd matrix. The diameter of the mixing disk was 20 mm, the mixing container was a beaker of 100 cm³ ($\phi = 40$ mm) and the speed was adjusted at 10000 rpm. The solution was added dropwise to the matrix during 3 minutes and the resulting mixture was stirred for 3 further minutes. The temperature attained during the emulsification is about 80 °C. The sample was stored for 5 days at room temperature in order to release all the air bubbles.

Viscoelastic measurements

- the samples were tested on a large frequency range with 2 rheometers:
 - a Carrimed rheometer (0.1 to 10 Hz)
 - a Metravib viscoelasticimeter (5 to 250 Hz).
- the deformation imposed was about 10 milliradians (Carrimed) and 10 μm (Metravib), in order to remain in the linear viscoelastic range.
- all samples were tested at 21 °C \pm 0.5.

We decided to begin by studying the influence of two parameters on the viscoelastic properties of an emulsion:

- *the volume fraction ϕ of the dispersed phase*
- *the ageing time of the emulsion.*

3.1. Influence of the volume fraction

The alkyd resin alone and 3 emulsions were tested.

- emulsion 1: volume fraction of the droplets 10 %
- emulsion 2: volume fraction of the droplets 20 %
- emulsion 3: volume fraction of the droplets 30 %

Results at low frequency

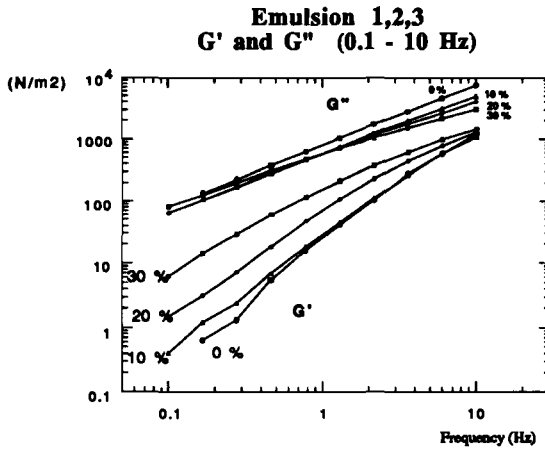


Fig.1: storage modulus (G') and viscous modulus (G'') of the pure alkyd and emulsions.

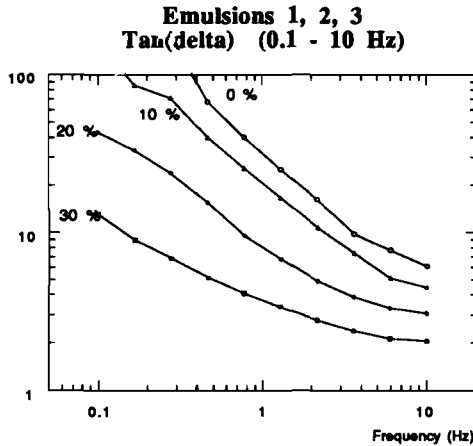


Fig. 2: loss tangent ($\tan\delta$) of the pure alkyd and emulsions.

As expected, the introduction of water droplets in the alkyd matrix produced a drastic modification of the storage modulus of the alkyd (figs.1 and 2). When the volume fraction of the droplets was increased, the elasticity of the emulsion also increased at low frequency (decrease of the loss tangent). One can see that all G' curves meet near 10 Hz. This result is confirmed in the study at high frequency (fig. 3) where crossing occurs.

Results at high frequency

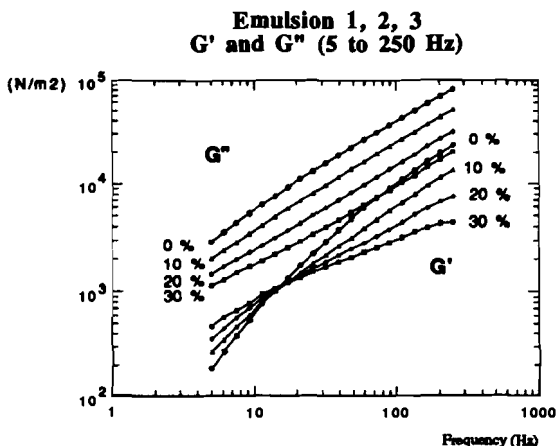


Fig. 3: storage modulus (G') and viscous modulus (G'') of the pure alkyd and emulsions.

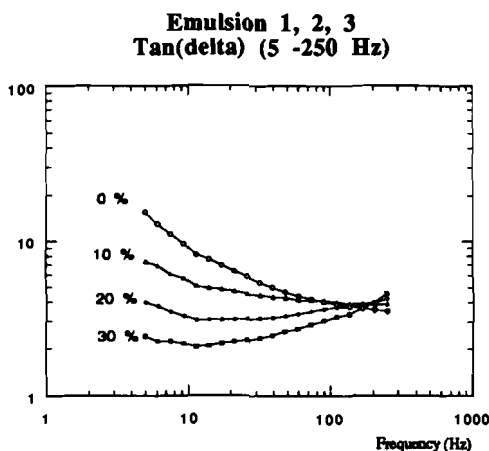


Fig. 4: loss tangent ($\tan\delta$) of the pure alkyd and emulsions.

At high frequency, both G' and G'' were found to decrease when the volume fraction was increased. The slopes of the storage modulus curves decreased dramatically when the volume fraction was increased (Fig. 3). A kind of relaxation plateau appeared beyond 10 Hz, which was more pronounced at high volume fractions. It is interesting to note that the presence of the droplets has the same effect on the storage modulus and on the viscous modulus: it decreases both moduli proportionally, that is why the differences in the loss tangent values referred to the pure alkyd and the 3 emulsions are very small around 200 Hz. This behavior assimilates the droplets to "holes" in the alkyd matrix at those frequencies.

3.2. Influence of the ageing time

The viscolastic properties of the emulsions were measured after 6, 12, 26 and 43 days respectively, in order to test the influence of the ageing time. It is important to underline that the emulsions did not show any phase separation within months of their preparation.

Results at low frequency

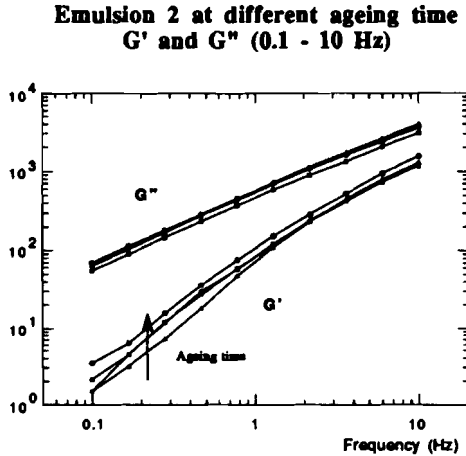


Fig. 9: storage modulus (G') and viscous modulus (G'') of the emulsion 2 (20 %) after different ageing times.

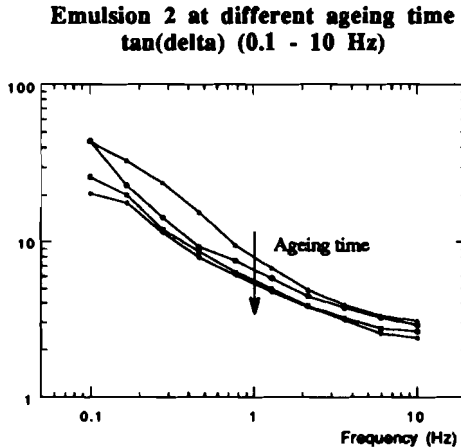


Fig. 10: loss tangent ($\tan \delta$) of the emulsion 2 after different ageing times.

The effect of the ageing time on the emulsion is appreciable at low frequency (figs. 9 and 10). An "old" emulsion is more elastic than a fresh one

Results at high frequency

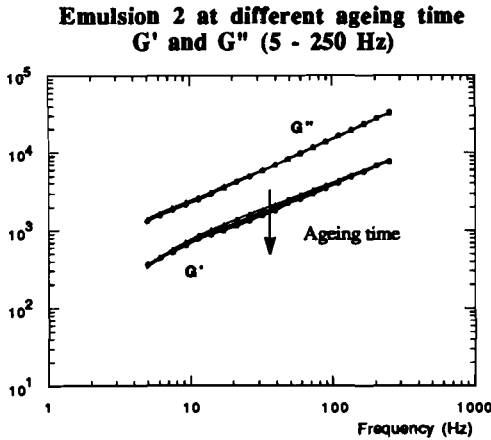


Fig. 11: Storage modulus (G') and viscous modulus (G'') of the emulsion 2 at different ageing times.

At high frequency (fig. 11) the differences observed are too small to be meaningful in terms of ageing time.

4. Discussions

We used the Palierne model (1990) in order to interpret our results. First, the theoretical curves for the emulsions were constructed:

- the disperse phase was considered as a purely viscous liquid:

$$G_i^* = i \cdot \omega \cdot \eta \quad \text{with } \eta = 10^{-3} \text{ Pa.s}$$

- the matrix was considered as a viscoelastic fluid (Maxwell model with a single relaxation time):

$$G_m^* = \frac{i \cdot \omega \cdot \eta}{1 + i \cdot \omega \cdot \lambda} \quad \text{with } \eta = 100 \text{ Pa.s and } \lambda = 10^{-6} \text{ s.}$$

- Influence of the ratio interfacial tension / radius of the droplets

Increasing the interfacial tension or decreasing the radius has exactly the same effect (Fig. 6,7,8). When the ratio γ / R is increased, not only the elasticity at a given low frequency decreases but the relaxation time of the droplets decreases correspondingly (i.e. the frequency at which the plateau begins increases). These phenomena give rise to typical crossing in the different G' and $\tan\delta$ curves, respectively.

Decreasing γ or increasing R "retards" the relaxation process of the droplets.

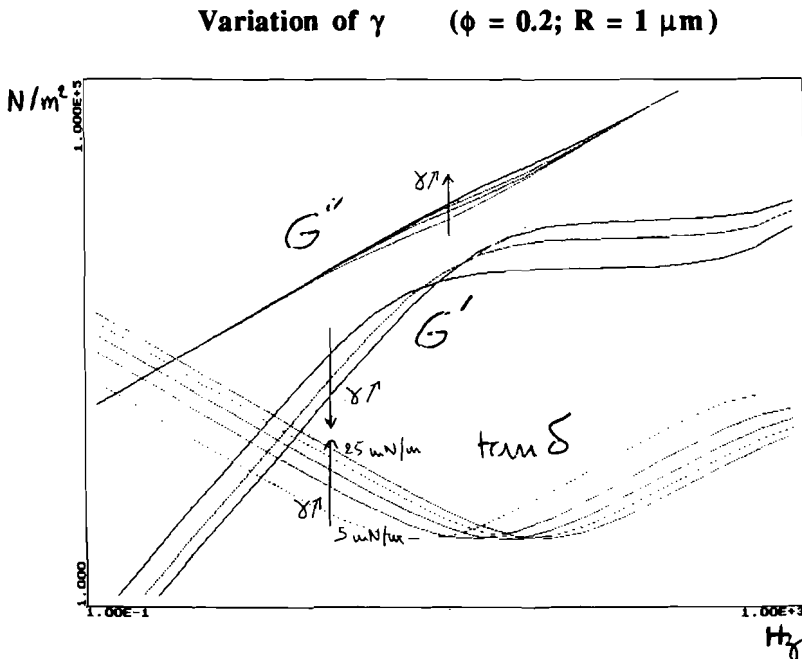


Fig. 6: theoretical curves of G' , G'' and $\tan\delta$ of emulsions; influence of the interfacial tension.

The influence of the variation of the volume fraction, the size of the droplets and the interfacial tension were analyzed theoretically (figs. 5, 6, 7, 8).

4.1. Theoretical curves (Palierne model)

- Influence of the volume fraction

At low frequency, the storage modulus was dramatically enhanced when the volume fraction increased. Interestingly, the G' curves do not cross each other on our frequency range, which implies that the beginning of the relaxation plateau occurs at the same frequency for all volume fractions (Fig. 5). This plateau is well defined on the theoretical curves above 10 Hz. The increase in elasticity at low frequency and this relaxation plateau suggest that the deformation of the droplets gives rise to a relaxation process (Palierne, 1990). In other words, the interfacial tension obliges the deformed droplets to return to their original shape. The frequency at which the plateau begins is the reciprocal relaxation time of the droplets. It is important to note, that the beginning of this plateau is well correlated with the minimum of the $\tan\delta$ curves.

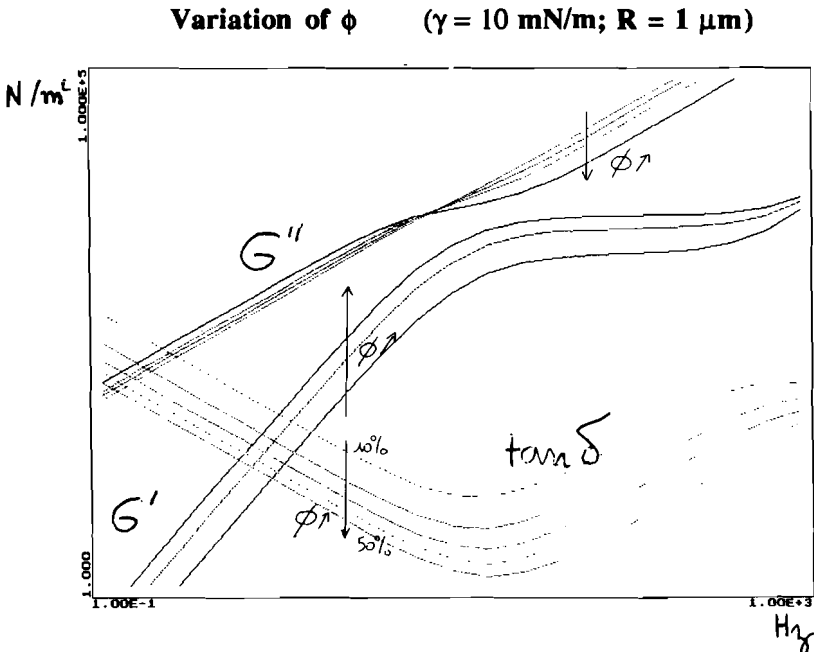


Fig. 5: theoretical curves of G' , G'' and $\tan\delta$ of emulsions; influence of a variation of volume fraction of the droplets.

Variation of R ($\gamma = 10 \text{ mN/m}$; $\phi = 0.2$)

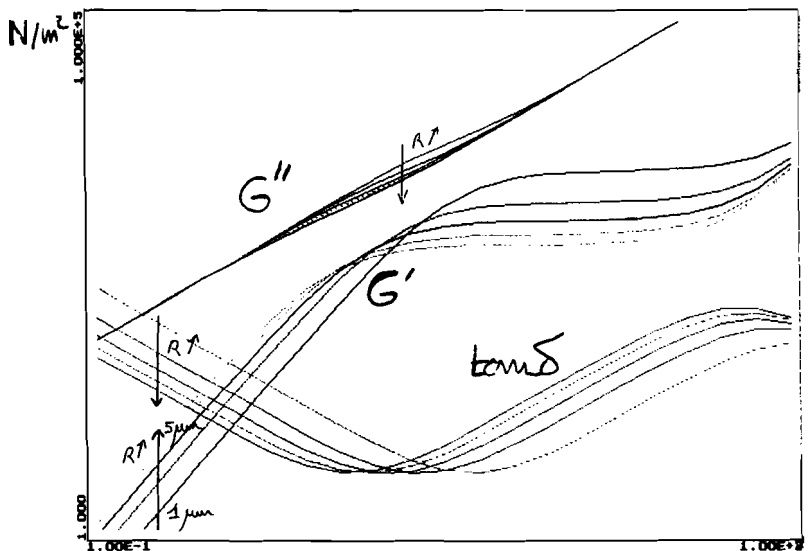


Fig. 7: theoretical curves of G' , G'' and $\tan\delta$ of emulsions; influence of the radius of the droplets.

Variation of γ / R ($\phi = 0.2$)

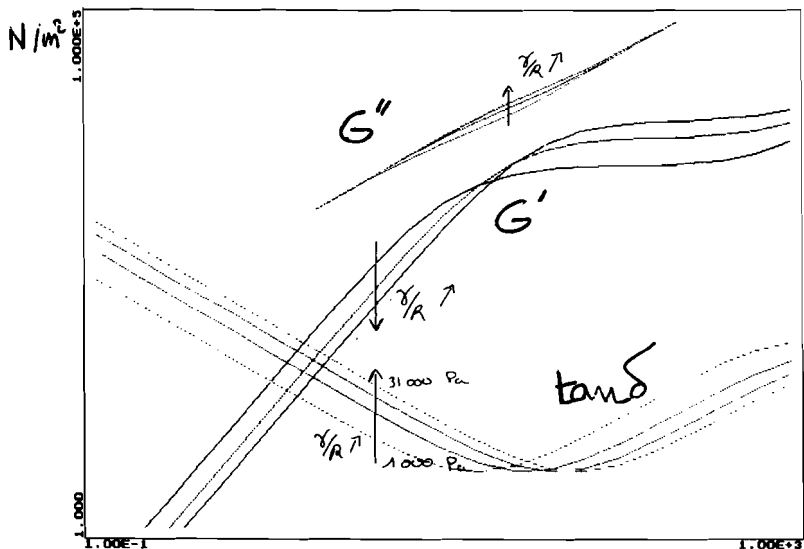


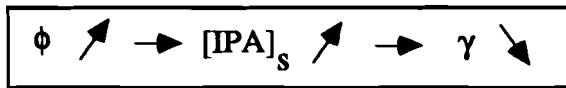
Fig. 8: theoretical curves of G' , G'' and $\tan\delta$ of emulsions; influence of the ratio γ / R .

4.2. Interpretation of the experimental curves

4.2.1. Influence of the volume fraction

The comparison of the shape of the experimental and theoretical curves (figs. 1, 2, and 5, 8) showed qualitatively that an increase in the volume fraction ϕ induces not only an increase of the elasticity at low frequency but also a decrease in the γ / R ratio which results in a crossing of the G' curves and in higher relaxation times at higher volume fractions (minimum in $\tan \delta$ curves in fig. 4).

The decrease of γ when ϕ is increased can be explained in terms of a change in the interfacial concentration of isopropanol $[IPA]_s$. Indeed, using the partition coefficient of isopropanol molecules between oil and water (Harris, 1947) and the Gibbs relation applied to the water / oil interface (Davies, 1963), calculations show an increase in the concentration of isopropanol at the interface when ϕ is increased. This in turn produces a decrease of γ .



4.2.2. Influence of the ageing time

In the same vein, the increase in elasticity at low frequency must be viewed as a consequence of the decrease of the γ / R ratio when ϕ is kept constant, because R may increase or γ may decrease, or both. The former possibility could be due to the coalescence of the droplets with time. This phenomenon would entail a decrease of γ in our system, because with a constant amount of isopropanol in the emulsion, the Gibbs relation predicts a decrease of its interfacial concentration when R increases. Thus, the increase of R induces a decrease of γ and consequently an important decrease of the γ / R ratio.

5. Conclusion and prospectives

Viscoelastic measurements on emulsions appear to provide meaningful results concerning their interfacial properties. The Paliarne model turned out to be a good tool for the qualitative interpretation of the experimental results.

This study underlines the important role of the ratio γ / R on the viscoelastic properties of an emulsion. It is now important to develop this method further towards a quantitative approach. If the radius of the droplets is better characterized, one could hope to be able to determine interfacial tensions directly in the emulsions, even at high viscosities and thus without having to dilute the vehicle. The relevance of these investigations to the role of the Fountain Solution and towards a better understanding of the transfer mechanisms in the lithographic process seem quite obvious.

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