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Small-angle neutron scattering study of a world-wide known emulsion: Le Pastis

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Abstract

'Pastis' is a famous aniseed based beverage, symbolic of hot summer days in the south of France. But who really knows the origin of the milky color when adding water? Each time you drink a glass of 'Pastis', you observe a complex phenomenon in physical chemistry! Pastis is mainly composed of anethol, an aromatic molecule, water, ethanol and additive compounds that improve the taste. Anethol has a very low solubility in water and further addition of water to the 'dry' preparation induces the formation of an emulsion made of large anethol droplets in a water-plus-ethanol solvent that scatter light. The origin of the spontaneous formation of the emulsion is a well-known phenomenon, which appears in liquid systems with three or more compounds, when the sample composition is trapped between the binodal and spinodal curves on the phase diagram. The radius of the droplets has been determined using the small-angle neutron scattering technique (D22, Institut Laue-Langevin, Grenoble). Of the order of a micron, the droplet size depends on the anethol/ethanol volume ratio and grows with time and temperature.
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1. Introduction

Pastis is an aniseed tasting beverage, served as aperitif as a short or long drink or used in mixed drinks and cocktails, and is very popular in the south of France especially during the warm summer days. All over the Mediterranean basin beverages of same family are drunk under the names of 'Ouzo' in Greece, 'Raki' in Turkey or 'Sambuca' in Italy. In the early part of the 1900s, the abuse of 'Absinthe' and its side effects on health led to it being forbidden in the USA, France and other European countries. In addition to the aniseed taste, the common feature of these drinks is the appearance of a milky aspect (Fig. 1a) after dilution with water, which is the aim of the present study.

When light falls on an object, it excites the electrons, brings them into oscillation and they radiate. For a perfectly homogeneous medium without local variation of the refractive index on the scale of the wavelength of light, the secondary waves interfere destructively except in the original direction of the light. The medium appears transparent and the incident beam is only visible by

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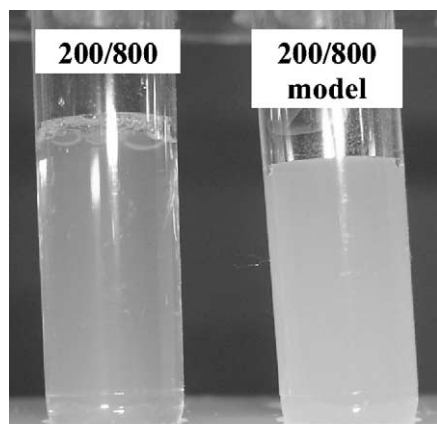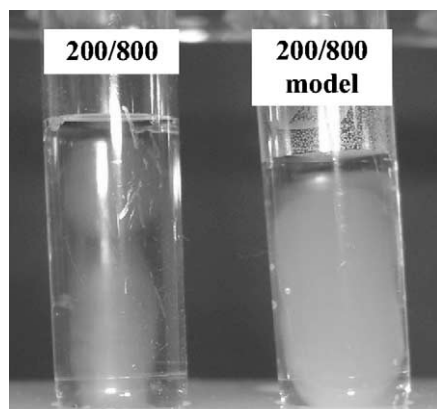
Fig. 1. Aspect of the samples '200/800' (left hand tube) and '200/800 model' (right hand tube) at room temperature as a function of time after preparation. (a) 10 min after preparation; (b) 10 h after preparation.

looking in the forward direction. Now, if the medium has heterogeneities with typical sizes of the order of the light wavelength, light radiation is scattered into all directions and the medium appears cloudy. Like clouds in the sky, smoke and dust in air or milk, a glass of Pastis scatters the light because it contains heterogeneities with typical size close to the light wavelength.

Complementary to light scattering, small-angle neutron scattering (SANS) is a powerful tool to explore the shape and size of heterogeneities in matter with typical sizes from a few angstroms up to thousands of angstroms. Neutrons are sensitive

to the nucleus of the atoms and an unique feature is the possibility of molecular labeling or contrast variation by replacing light water by heavy water for example. Thus, Pastis was diluted with D_2O instead of H_2O, which makes the beverage undrinkable and toxic for cell metabolism but perfect for a SANS experiment.

The principal aromatic molecule of Pastis is 1-methoxy-4-(1-propenyl)benzene commonly called trans-anethol (Fig. 2) naturally present in star aniseed or fennel seeds. Known since Antiquity for its therapeutic properties, the molecule is still widely used as flavoring for foods and beverages or in creams and perfumes. The essential oil is extracted by steam distillation. Above 23 °C, it is a colorless or faintly yellow liquid soluble in absolute ethanol but nearly insoluble in water (few mg l^{-1}). In the 'dry Pastis', the amount of water is sufficiently low and anethol remains solubilised in the water/ethanol mixture. But further addition of water induces the formation of an emulsion of anethol droplets in a (water+ethanol) continuous medium.

This phenomenon is well known in ternary liquid mixtures such as for example ethanol/toluene/water [1] or styrene/methanol/water, where it is used to produce monodisperse latex particles [2]. It has been the object of a recent article and called the 'Ouzo effect', from the name of the Greek beverage [3]. We consider a ternary liquid system composed of oil and two solvents, one of them being water. We suppose that the oil is nearly insoluble in water, but completely soluble in the second solvent and that the two solvents are miscible in all proportions. On the phase diagram, the binodal curve defines the thermodynamic minima in the Gibbs free energy of the system (as a function of temperature or mole fraction) and corresponds to the miscibility limit. The spinodal
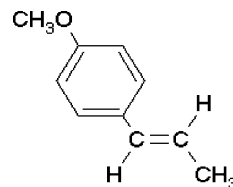

Fig. 2. Structural formula of the anethol molecule.

curve traces the limit of thermodynamic stability. Inside the area delimited by the spinodal, the system will spontaneously and rapidly separate into two phases with compositions on the binodal curve. Between the binodal and the spinodal, a system can exist for long time in a metastable state where the Gibbs free energy is not minimized [4]. When a single-phase solution of the ternary system is rapidly brought into the metastable state by addition of water, the solvent mixture becomes supersaturated in oil. Nuclei form spontaneously from small local fluctuations in oil molecule concentration in a process called homogenous nucleation. A homogenous dispersion of small droplets with typical diameter of the order of the micrometer and relatively monodisperse in a continuous liquid phase is formed within milliseconds or less. Then, further growth of the droplets occurs by Oswald ripening at relatively slow rates, since the dissolution and diffusion rates of the oil molecules are small (around 10^{-5} cm^2 s^{-1}) [3]. Because emulsions are in a non-equilibrium state, the droplet size and number depend not only on variables such as temperature or composition but also on the method of preparation [5].

2. Materials and methods

2.1. Sample composition and preparation

Commercial Pastis is composed mainly of 2 g l^{-1} of anethol in 45 vol.% of ethanol and 55 vol.% of H_2O (Table 1). Up to 26 other components (aromatic molecules, fatty acids, esters...) present in very small quantities have been identified in 'Ouzo' products [6]. Used to improve the taste, these molecules are also a trade secret and we will neglect their contribution to the emulsion formation. In parallel, we modeled the commercial Pastis

with a pseudo-ternary system made of anethol/ethanol/($D_2O + H_2O$). Anethol was purchased from Fluka, with purity higher than 99% and used as received. Absolute ethanol was obtained from Prolabo. Physical parameters of the molecules used to prepare the samples are summarized in Table 2.

It is recommended by the manufacturer to dilute one volume of Pastis with at least 5 volumes of water. Thus two concentrations 10 and 20 vol.% in D_2O were studied to investigate the role of dilution on the size of droplets. In the following, the two samples prepared from the commercial beverage are called '100/900' and '200/800', respectively. For the model samples, a first solution of 0.451 vol.% of anethol in ethanol was prepared (Table 3a). Two water solutions were prepared to reproduce exactly the proportions of light and heavy water in the '100/900' and '200/800' samples (Table 3b). The water solution 1 (or 2) was then added to the anethol/ethanol solution in the required proportions (Table 3c). These two samples were called the '100/900 model' and the '200/800 model'. The final volume fractions are given in Table 4.

Finally, a concentrated solution of 0.894 vol.% of anethol in ethanol (Table 3a) was prepared to investigate the influence of the ratio anethol/ethanol on the droplet size. Diluted in same way as the '200/800 model' (Tables 3c and 4), we called this sample the '200/800 concentrated'.

In the model samples, the white milky color appeared immediately after addition of water to the anethol/ethanol mixture (Fig. 1a). The samples were loaded into 2 mm rectangular Hellma cells and installed in the sample changer where the temperature was controlled using a circulating water bath.

Table 1
Composition of 'commercial dry' Pastis in the bottle

Composition	H_2O	Ethanol	Anethol
Vol.%	54.8	45	0.2
Density	0.8107		

Table 2
Physical parameters (molar mass, density and scattering length densities) of molecules present in the samples

	H_2O	D_2O	Ethanol	Anethol
M (g mol^{-1})	18	20	46.07	148.21
Density	1	1.1044	0.81	0.98
ρ (cm^{-2})	-5.59×10^9	6.38×10^{10}	-3.54×10^9	1.09×10^{10}

Table 3a
Stock solutions of anethol in ethanol

	Anethol	Ethanol
Solution 1		
Φ vol.%	0.451	99.549
Solution density	0.8107	
Concentrated solution		
Φ vol.%	0.894	99.106
Solution density	0.8116	

Table 3b
Volume fractions H_2O/D_2O used for preparation of the '100/900' and '200/800' samples

	H_2O	D_2O
Water solution 1 for '100/900'		
Φ vol.%	5.74	94.26
Solution density	1.0984	
Water solution 2 for '200/800'		
Φ vol.%	12.05	87.95
Solution density	1.0918	

Table 3c
Preparation of the model samples '100/900', '200/800' and '200/800 concentrated'

'100/900 model'	Anethol in ethanol solution 1	Water solution 1
Φ vol.%	4.5204	95.4796
'200/800 model'	Anethol in ethanol solution 1	Water solution 2
Φ vol.%	9.0408	90.9592
'200/800 concentrated'	Anethol in ethanol, concentrated solution	Water solution 2
Φ vol.%	9.1461	90.8539

In a first experiment, we focussed on the effect of time on the droplet size. The sample temperature was kept at 20 °C and measurements were made at regular time intervals. The aim of a second experiment was to study the effects of temperature. As the initial emulsion may depend on the preparation, we worked with the same sample and increased the temperature. In these conditions the combined effects of time and temperature were seen. Temperatures between 10 and 38 °C were chosen and we waited for 30 min for temperature equilibration between each temperature increment.

2.2. Small-angle scattering experiments

Since the samples scatter light, large droplets are formed and low q-vectors are required for the neutron scattering experiments. Experiments were carried out on the instrument D22 at the Institut Laue-Langevin (Grenoble). With its large dynamic q-range covered in only one setting, the very high flux and the low background, D22 is the most powerful SANS instrument in the world [7]. Two configurations were used to cover a q-range from 10^{-3} to 5.6×10^{-2} Å^{-1}. The small angle configuration was obtained with $\lambda = 15$ Å, sample to detector distance $D = 17$ m, collimation $C = 17.6$ m. The middle angle configuration ($\lambda = 15$ Å, $D = 5$ m, $C = 5.6$ m) was necessary to estimate the level of incoherent background. To obtain a good statistics, exposure times of 1 h and 30 min were necessary for the small and middle angle configuration, respectively. The raw data were radial averaged, corrected for electronic background and empty cell using standard ILL software. Particular care was taken for the normalization using water scattering because the radius calculated from a Porod's law depends on the accuracy of the absolute scale (Eq. (1)).

3. Results and discussion

A typical curve obtained with the emulsions of anethol in $(D_2O + H_2O)$/ethanol is shown in Fig. 3. The intensity in cm^{-1} is plotted vs. q for the sample '200/800 model' at 12 °C. One observes a strong scattered intensity at low q and the q^{-4} slope characteristic of a sharp interface between two media extends over four decades in intensity and one decade in q, from 2.5×10^{-3} to 2.5×10^{-2} Å^{-1}. With time and/or by increasing temperature a slight decrease of the intensity is observed reflecting the growth of droplets.

Table 4
Composition and scattering length densities of the different samples

	H_2O	D_2O	Ethanol	Anethol
Sample '100/900'				
Φ vol.%	5.4796	90	4.5	0.0204
Density	1.0854			
ρ Solvent (cm^{-2})	5.70×10^{10}			
$\Delta\rho$ (cm^{-2})	4.61×10^{10}			
Sample '200/800'				
Φ vol.%	10.9592	80	9	0.0408
Density	1.0664			
ρ Solvent (cm^{-2})	5.01×10^{10}			
$\Delta\rho$ (cm^{-2})	3.92×10^{10}			
Sample '200/800 concentrated'				
Φ vol.%	10.9582	79.9	9.06	0.0818
Density	1.0661			
ρ Solvent (cm^{-2})	5.01×10^{10}			
$\Delta\rho$ (cm^{-2})	3.92×10^{10}			
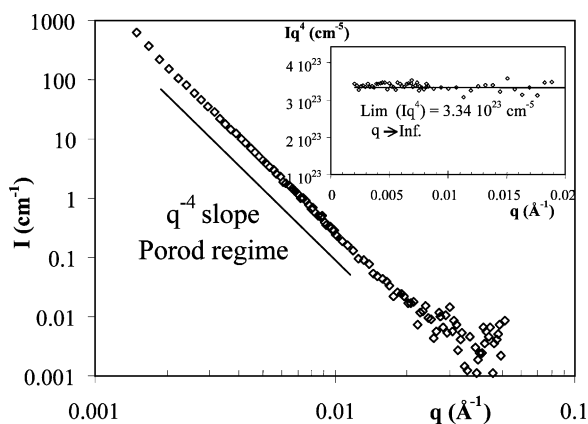
Fig. 3. Log–log plot of the absolute intensity vs. q for the sample '200/800' at 12 °C. This curve is typical of the SANS curves obtained by measuring emulsions of anethol in (D_2O + H_2O)/ethanol. Insert: Porod representation, Iq^4 vs. q.

3.1. Brief theoretical background

Assuming a sharp interface between two homogenous media, the specific area Σ of the interface can be measured using the Porod's limit [8]:

$$\Sigma(cm^2/cm^3) = \frac{1}{2\pi(\Delta\rho)^2} \lim(q \to \infty)I(q)q^4 \qquad (1)$$

Where $I(q)$, the scattered intensity is precisely known on an absolute scale (cm^{-1}) and $\Delta\rho$ is the difference of scattering length densities between anethol droplets and solvent (Tables 2 and 4). The use of D_2O instead of H_2O increases the contrast by a factor of 4 and reduces considerably the incoherent background. Assuming now a spherical geometry of the droplets and neglecting their polydispersity, the radius is deduced from the specific area Σ and the volume fraction Φ:

$$R = \frac{3\Phi}{\Sigma} \qquad (2)$$

An example of a Porod representation is presented in the insert in Fig. 3 (sample '200/800' at 12 °C). A straight line parallel to the q-axis is obtained over one decade and allows the extrapolation $\lim(Iq^4)(q \to \infty)$ and calculation of Σ from (Eq. (1)). In this example, one finds a specific area of $\Sigma = 34.58 \text{ cm}^2 \text{ cm}^{-3}$ and a radius of 0.354 μm.

The evolution of the radius as a function of time and temperature is summarized in Fig. 4a and b for the samples '100/900' and '200/800' and Fig. 5a–c for the samples '100/900 model', '200/800 model' and '200/800 concentrated'. The appearance of the samples as a function of time can be seen in Fig. 1b, where one observes the disappearance of the milky aspect 10 h after preparation.
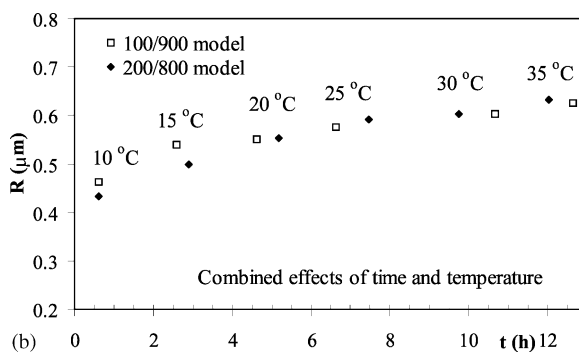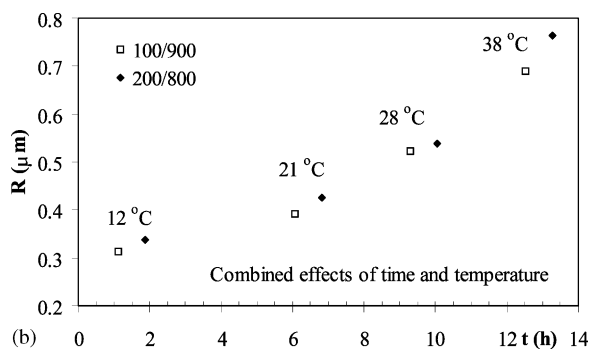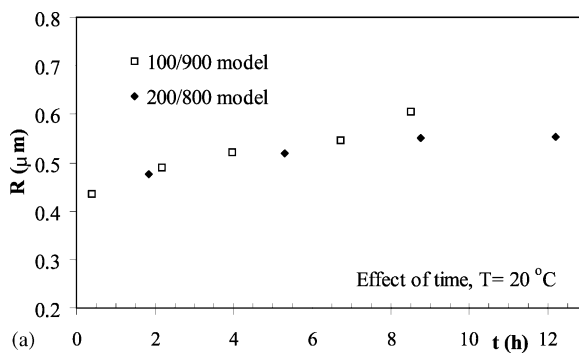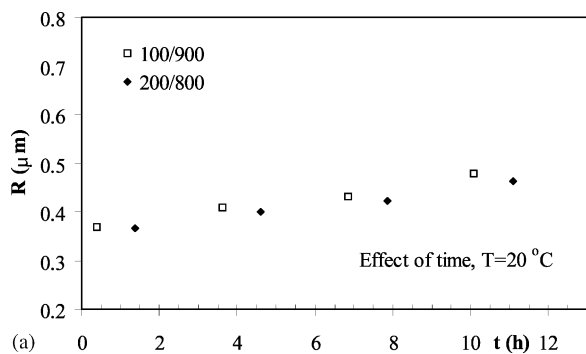
Fig. 4. Droplet radii for the '100/900' and '200/800' samples (a) as a function of time; (b) as a function of time and temperature.

If we compare the '100/900' and 200/800' samples, the radii do not depend significantly on the total volume fraction of anethol. Those obtained with the 'model' samples are slightly higher than the ones measured in the 'commercial' samples. For example, at 20 °C and 1 h after preparation, one finds $R = 0.477$ μm for the sample '200/800 model' and 0.365 μm for the sample '200/800'. Twelve hours after preparation, the droplet radius has increased of 0.15 μm on average in the '100/900' and '200/800' samples and 0.08 μm in the model samples.

The effect of temperature is much stronger than the effect of time alone and the commercial beverage is more sensitive to temperature than the model samples. Again, the droplet size does not depend significantly on the total anethol concentration and the '100/900' and '200/800' droplets grow in parallel. Combined effects of time and temperature (from 10 to 35 °C) induce increase in radius of 0.4 μm for the '100/900' and
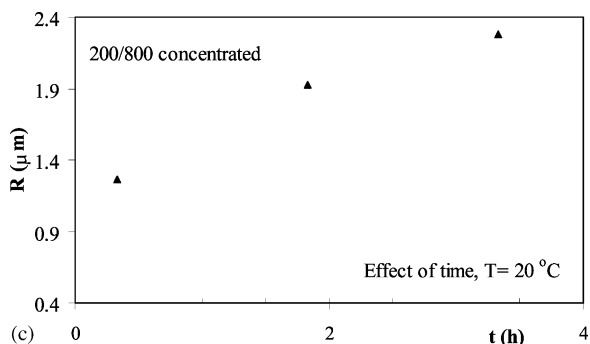

Fig. 5. Droplet radii for the model system (a) as a function of time; (b) as a function of time and temperature; (c) '200/800 concentrated' as a function of time.

'200/800' samples and of 0.15 μm only for the '100/900 model' and '200/800 model'.

When the anethol/ethanol ratio is increased, (sample '200/800 concentrated', Fig. 5c), the radius is significantly higher than that of the sample '200/800 model' ($R = 1.267$ μm after preparation) and is nearly doubled 3 h later. The temperature effect was not measured for this sample.

In [3], the authors demonstrated that the mean droplet diameter is a function of the oil-to-ethanol volume fraction. Our results are clearly consistent with this conclusion, since the two water dilutions at the same anethol/ethanol ratio did not change significantly the droplet radius, but multiplying the anethol/ethanol ratio by two increases the radius by a factor 3.

Coalescence and Oswald ripening are two possible mechanisms involved in the droplet growth. Coalescence implies the merging of the oil droplets to form larger ones. Oswald ripening is the growth of the larger droplet at the expense of the smaller one because of the higher solubility of the smaller and mass transport through the continuous phase [9–11]. The two processes can be distinguished in principle with their behaviours as a function of time. Coalescence is described by a linear increase of the logarithm of the mean droplet radius with time whereas Oswald ripening is characterized by a linear increase of the volume of droplets with time. Unfortunately, the few points available here are not sufficient to separate clearly the two models.

The role of temperature is a delicate problem due to the temperature dependence of a number of parameters. Solvent viscosity, diffusion coefficient, solubility of oil and surface tension between oil and solvent are the main parameters involved in these two processes and are temperature dependent. Unfortunately, little is found about the properties of the anethol molecule in the literature.

Both the size of the droplets and the density difference between the oil and the continuous phase determine the stability in time of such a metastable emulsion. If the density of the droplets is close to that of the continuous phases and if the droplets are small, bulk phase separation by creaming will be slowed down. Replacing H_2O by D_2O in our experiments has increased the difference of density between anethol droplets and the continuous medium and thus has certainly enhanced the droplet ripening.

The stability of beverage emulsions and their shelf life are a major question in food chemistry. Most beverage emulsions are composed by flavor oil, water, ethanol (if alcoholized) and moreover hydrocolloids like gum arabic are added to improve emulsification and stability. In spite of the additive, the dilute emulsions evolve towards phase separation. In [12], the authors measured an increase of the creaming rate by a factor of 10 by increasing the temperature from 4 to 55 °C. This result is in agreement with the faster growth of anethol droplets with temperature. In the same article, it was demonstrated that Oswald ripening was the dominating mechanism during the emulsion aging.

4. Conclusion

Many phenomena observed in daily life are explained on the basic rules of physical chemistry. Pastis is an emulsion formed of anethol droplets with diameter of the order of the micrometer, dispersed in a continuous medium of water and alcohol. As with any emulsion, the droplets grow with time and temperature; the preparation tends towards phase separation. The commercial system forms smaller droplets that are much sensitive to temperature. The difference between the two systems comes probably from the molecules added by the manufacturer in the commercial beverage. More systematic studies would be necessary to compare the experimental growth of the anethol droplet with models like Oswald ripening or coalescence, but this falls outside the scope of the present paper. In conclusion, never change a 'proven' tradition; enjoy your cool drink without waiting!

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