

## Formulation–composition map of a lecithin-based emulsion

Rajeev K. Thakur<sup>a</sup>, C. Villette<sup>b</sup>, J.M. Aubry<sup>b</sup>, G. Delaplace<sup>a,\*</sup>

<sup>a</sup> UR 638, Génie de Procédés et Technologies Alimentaires, INRA, 369 rue Jules Guesde, B.P. 39, F-59651 Villeneuve D'Ascq, France

<sup>b</sup> LCOM, Equipe "Oxydation et Formulation", UMR CNRS 8009, ENSCL BP 90108, F-59652 Villeneuve D'Ascq, France

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### Abstract

Formulation–composition map is an interesting tool to predict the nature of an emulsion, stability, viscosity and nevertheless to decide the mixing protocol of its ingredients. Information based on optimum formulation (environmental conditions at which the affinity of an emulsifier for oil and for aqueous phase is same), which is depicted through hydrophilic–lipophilic deviation (HLD) concept, is necessary to make a formulation–composition map of an emulsion. In order to apply this concept in food emulsions, it is necessary to determine characteristic constants of each component of the system, i.e. the aqueous phase, the oil phase and the emulsifier at equilibrium. In this work formulation–composition map of a sunflower oil–water–lecithin system, based on the knowledge of phase behavior of lecithin at equilibrium and emulsification, was made. The shape of inversion line on formulation–composition map was not the classical stair type rather an almost vertical inversion line at water-fraction ( $f_w$ ) near 0.20 was observed. It was supposed to be linked to the viscosity of oil phase which was 50 times the viscosity of aqueous phase. Additionally, emulsions were of oil-in-water (O/W) type for  $f_w$  higher than 0.20, but their viscosity and the drop size behavior with respect to salt concentration as formulation variable did not show the existence of transitional inversion line on formulation–composition map. Such map in advance can certainly facilitate the guidelines for dynamic emulsification.

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**Keywords:** Food emulsion; Hydrophilic–lipophilic deviation (HLD); Lecithin; Phase inversion; Sunflower oil

### 1. Introduction

Although emulsions are the systems out of equilibrium, still physico-chemical formulation at equilibrium can be well correlated to the emulsion properties, e.g. viscosity, stability, drop size. Recently Salager [1] has shown the importance of phase behavior through the citation of Laughlin: "an independent determination of the equilibrium phase behavior is essential if one has to diagnose correctly the kinetics and colloidal phenomena that exist". Formulation parameters, i.e. types of emulsifiers and oils, types of salts, alcohols and their concentration, temperature play a role in equilibrium phase behavior. For instance, an increase of temperature can modify the affinity of emulsifier from water-to-oil which gives a concept of phase inversion tem-

perature (PIT) in emulsion making. Knowledge of equilibrium phase behavior of an emulsion system, i.e. oil–water–emulsifier has proven to be an interesting tool to study emulsification process as far as drop size and stability of an emulsion is concerned [1–3]. However, majority of the concepts developed in emulsion area are focused to emulsifier's characteristics, e.g. HLB number, packing parameter, solubility. On the other hand, the affinity of an emulsifier for oil or water depends on formulation parameters and they are taken into account by a concept called hydrophilic–lipophilic deviation (HLD) concept. It was developed in the 1980s in order to understand the effects of emulsion's environment on emulsion properties in pharmaceuticals, cosmetics and for enhanced oil recovery [4]. From the immense work on phase behavior of oil–water–emulsifier system, empirical equations were proposed for ionic as well as non-ionic emulsifiers. For non-ionic emulsifiers, HLD is written as:

$$\text{HLD} = (\alpha\text{-EON}) + bS - k\text{EACN} + aA + t\Delta T \quad (1)$$

This number can be positive or negative which signifies the emulsifier's affinity for oil or water phase respectively. This concept is very similar to Winsor  $R$  ratio. The value of HLD equal

*Abbreviations:* EACN, equivalent alkane carbon number; EON, ethylene oxide number; HLD, hydrophilic–lipophilic deviation; O/W, oil-in-water emulsion; o/W/O, oil-in-water-in-oil emulsion, multiple emulsion; PC, phosphatidylcholines; W/O, water-in-oil emulsion; w/O/W, water-in-oil-in-water emulsion, multiple emulsion

\* Corresponding author. Tel.: +33 320435437; fax: +33 320435426.

E-mail address: [delapla@lille.inra.fr](mailto:delapla@lille.inra.fr) (G. Delaplace).

### Nomenclature

$a$	constant depends on type of alcohol
$A$	concentration of alcohol (%w/v)
$b$	constant depends on type of salt
$d$	diameter of droplets (m)
$d_{43}$	volume average diameter of droplets (m)
$f_w$	volume fraction of water in an emulsion
$f_{wc}$	critical volume fraction of water
HLD	hydrophilic–lipophilic deviation number
$k$	constant depends on type of emulsifier
$k_B$	conductivity of emulsion ( $\text{mS cm}^{-1}$ )
$k_w$	conductivity of aqueous phase ( $\text{mS cm}^{-1}$ )
$S$	salt concentration in aqueous phase (%w/v)
$t$	constant depends on the type of emulsifier
$\Delta T$	temperature difference with respect to $25^\circ\text{C}$
$x$	volume fraction of sunflower oil in total volume of oil

### Greek letters

$\alpha$ -EON	constant depends on the type of emulsifier
$\mu$	viscosity of emulsion ( $\text{Pa s}$ )
$\dot{\gamma}$	shear rate ( $\text{s}^{-1}$ )

to zero means Winsor III state in phase diagram, i.e. formation of microemulsion. This state is also called as optimum formulation.

When HLD is coupled with the composition (volume fraction of water in oil–water system), a two dimensional map is constructed called formulation–composition map. It is frequent that above 75% of the dispersed phase the formulation (i.e. HLD) does not govern the type of emulsion it should form. On this 2D map the boundary which separates the morphology of one type of emulsion to other normally forms a stair like structure. A typical example of formulation–composition map of an emulsion system is shown in Fig. 1. The vertical line below and above the  $\text{HLD}=0$  is known as catastrophic inversion line, while the horizontal line ( $\text{HLD}=0$ ) is transitional inversion line. The knowledge of catastrophic inversion line appears in dynamic

condition, i.e. while making of emulsion, but transitional inversion line is the result of phase behavior of oil–water–emulsifier system at equilibrium. Such a map is advantageous for formulation protocol of an emulsion to get the desired properties in a predictive and more controlled way.

In food emulsion systems, such map is rare due to complexities associated with (i) emulsifiers (phospholipids or proteins) and (ii) oil phase (mostly triglycerides). The phase behavior at equilibrium of even a simple food emulsion system is not easy to observe. It is well known that triglycerides are poorly soluble [5]. Consequently, they form microemulsions not as much in amount as oils containing short chain fatty acids [6–8]. Furthermore, the interfacial region may contain a mixture of surface-active components including proteins, phospholipids, alcohol and particles. In addition, these components may adopt various conformations or structures in oil, water or interfacial region, which also depends on external factors such as temperature and mechanical agitation. Consequently, food emulsion systems might not have the same phase behavior as petroleum emulsions. Hence, these complexities with food emulsion system restrict the detection of optimum formulation by conventional means like visual observation, light scattering and interfacial tension measurements.

Recently, spectrophotometric method associated with formulation scan was proposed to get the knowledge of the HLD parameters of sunflower oil–water–lecithin system [9]. It is pre-requisite to make a formulation–composition map of an emulsion system. Therefore, in the context of food emulsions the objective of this study was to establish a formulation–composition map of a lecithin-based emulsion and to make a comparison with that of the non-food emulsions. In addition, few emulsions with different formulation and composition, e.g. near and far from catastrophic inversion (composition) and positive and negative HLD (formulation) were made to point out the feasibility of a formulation–composition map.

## 2. Materials and methods

### 2.1. Chemicals

Egg Lecithin (Ovothin 120) was used as an emulsifier which had iodine value 70. It was supplied by Degussa (France). The distribution of different components of Ovothin 120 according to manufacturer is as follows (w/w): 30% phospholipids, 63% triglycerides (egg oil), 5% cholesterol and 2% moisture. The majority of phospholipids were phosphatidylcholines (PC), 22% in Ovothin 120. Therefore, PC hereafter will be referred as lecithin. NaCl salt was used to vary the salinity of the oil–water–emulsifier systems. It was supplied by VWR BDH Prolabo (France). Sunflower oil was used as the source of oil phase which has viscosity 0.05 Pa s. This oil was purchased from a local supermarket. The water was purified double distilled Milli-Q (Millipore) water.

### 2.2. Emulsion preparation

For the preparation of emulsions, sunflower oil and lecithin were firstly mixed together in 50 mL tubes, thereafter, salted

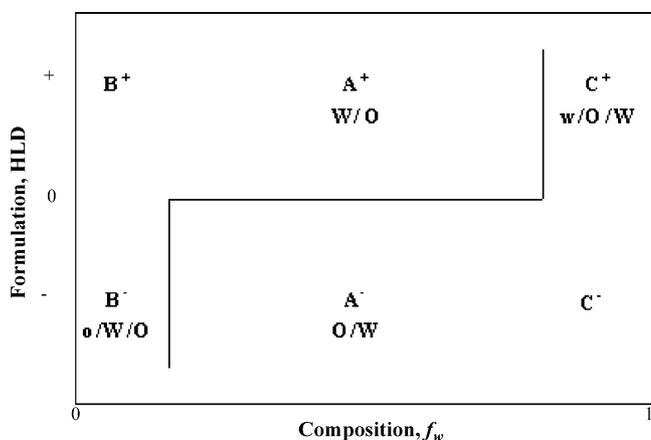


Fig. 1. A generalized formulation–composition map on two-dimensional plot [4].

Table 1  
HLD parameters of sunflower oil–water–lecithin system used as a model food emulsion system

Characteristics of ingredients		Value	References
Salt	$b$	0.13	Salager et al. [10]
Lecithin	$k$	0.13	Thakur et al. [9]
	$\alpha$ -EON	-0.25	
Sunflower oil	EACN	21.7	
Egg oil	EACN	-3.9	

water was added. The total volume of emulsion was 20 mL. The composition, i.e. fraction of water in total volume (water and oil) was varied from  $f_w = 0.1$  to  $f_w = 0.9$  with an interval of 0.1. The amount of lecithin was 5% (w/v) in each tube, which corresponds to that of a classical mayonnaise. The presence of egg oil coming with lecithin was taken into account in total volume of oil in a tube to know the volume fraction of water. The salinity and the water fraction of each emulsion were varied to produce a sequence of systems corresponding to different formulations and compositions. The different salinity of aqueous phase was 0.1, 1, 10, 20, and 30% of NaCl in water. This range of salt concentration covered the value so-called optimum formulation which was around 12% NaCl for this system in the absence of alcohol [9]. This calculated value is based on the characteristics of oils and lecithin (Table 1) determined elsewhere through formulation scans [9,10]. The tubes were left at constant temperature (25 °C) for 3 days to ensure physico-chemical equilibrium of the system. On the fourth day, equilibrated ingredients in the tube were mixed with a vortex mixer for 1 min to make an emulsion.

### 2.3. Conductivity measurement

The conductivity of an emulsion was instantly measured by conductivity meter SevenMulti™ (Mettler-Toledo GmbH, Switzerland) just after their formation. The value of the conductivity indicates the type of emulsions, oil-in-water (O/W) or water-in-oil (W/O). For instance, conductivity more than  $0.1 \text{ mS cm}^{-1}$  indicated that the water was the continuous phase and the oil was the dispersed phase, i.e. the type of emulsion is O/W emulsion. For the opposite case, i.e. for W/O type of emulsion, the conductivity was lower than  $100 \mu\text{S cm}^{-1}$ . For each sample the experimental conductivity was compared to Bruggeman's conductivity which is valid for polydispersed systems:

$$k_B = k_w (f_w)^{3/2} \quad (2)$$

where  $k_w$  is the conductivity of continuous phase in the absence of the dispersed phase and  $f_w$  is the fraction of dispersed phase in an emulsion. The deviation of experimental conductivity from the above one can present an insight over multiple or abnormal type of emulsions [1,11].

### 2.4. Microscopic analysis

Emulsions were observed at micro-level through an optical microscope Olympus-BH2 (Olympus Optical Co. Ltd., Japan)

and photographed through a digital camera to compare the drop size and their distribution. The emulsion was put in to a uniform gap of 1 mm made on a glass plates.

### 2.5. Drop size measurement

The mean drop diameter and volume distribution of droplets were measured by particle size analyzer Mastersizer-MSS (Malvern Instruments Ltd., UK) at 25 °C. The measurements were done only for O/W type of emulsions.

### 2.6. Rheology

The flow curve of emulsions was made using a cone-plate geometry of stress controlled rheometer Rheolyst AR 1000 (TA Instruments, USA) in the range of  $1\text{--}1000 \text{ s}^{-1}$  shear rate. All samples were analyzed at 25 °C.

## 3. Results and discussions

### 3.1. Formulation–composition map

Morphology of emulsions was determined by conductivity measurement of an emulsion. Based on the types of emulsions, formulation–composition map was established as shown in Fig. 2. The results concerning the frontier are discussed below.

Emulsions were prepared for a range of salt concentration and composition. As an example, the conductivity of emulsions of different composition for 10% salt is shown in Fig. 3. The transition of emulsion from O/W to W/O with respect to  $f_w$  was detected by a sharp decrease of conductivity. And, therefore, the border between O/W and W/O was determined for each salt concentration. Conductivity of emulsions was always lower than that of theoretical (according to Bruggeman's law) one as calculated by Eq. (2). This deviation of conductivity was always between 20 and 30% depending on  $f_w$ . In few studies this deviation is an indication of formation of multiemulsion, the type w/O/W. There, a few percentage of water is inside the oil droplets [1,11].

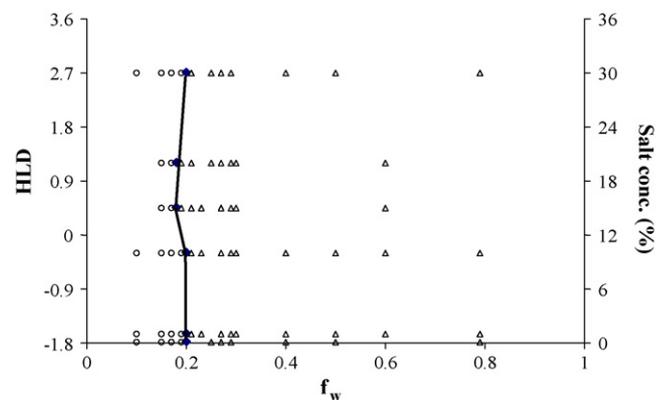


Fig. 2. Formulation–composition map of sunflower oil–water–lecithin emulsion system based on types of emulsions produced in a tube with a vortex mixer at 25 °C, (○) W/O and (△) O/W.

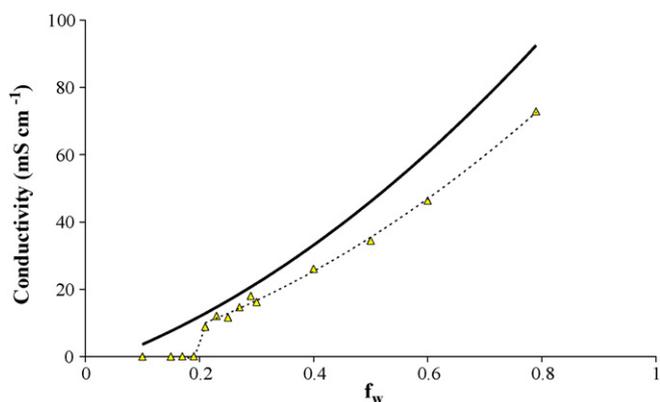


Fig. 3. Conductivity of emulsions ( $\Delta$ ) compared with one calculated (continuous line) from Bruggeman's law for 10% of salts at 25 °C.

As the HLD parameters of sunflower oil–water–lecithin were known [9], therefore different concentration of salt could be presented on HLD scale through following equation:

$$\text{HLD} = (\alpha - \text{EON}) + bS - k\{xEACN_1 + (1 - x)EACN_2\} \quad (3)$$

where  $x$  and  $(1 - x)$  are the volume fraction of sunflower oil and oil in egg lecithin. It should be noted that the HLD scale is developed for  $f_w = 0.5$  where  $x$  corresponds to 0.676 with lecithin concentration of 5% (w/v).

In Fig. 2, the vertical line indicates the catastrophic inversion line. It appears that the catastrophic inversion line in positive and negative HLD zone are not very different (for  $\text{HLD} > 0$ ,  $f_{wc}$  is 0.18 and for  $\text{HLD} < 0$ ,  $f_{wc}$  is 0.20). A little deviation was found near  $\text{HLD} = 0$ . Such deviation is not very important statistically but in catastrophic inversion theory, a difference of 0.02 has significance. The left zone of the inversion line always resulted W/O type of emulsion while right O/W type. The critical water fraction should be compared to the maximal packing of monodisperse hard spheres, which is 74% (v/v). Here, the dispersed phase (oil) volume fraction reached 80% in water as continuous phase. This may be explained by the polydispersity of the oil droplets dispersed in the water as continuous phase. This polydispersity allows achieving such a low  $f_w$  for O/W emulsions because comparatively smaller droplets submit themselves in the void volume of the larger ones. This can be confirmed through visual observation using an optical microscope and by

particle size distribution measurements. The volume distribution of particles showed two peaks. They will be discussed in next section.

A comparison of formulation–composition map in Fig. 2 with that of emulsions of cosmetics and petroleum grade (Fig. 1) for example 4 wt% Span-Tween mixtures, kerosene, 1 wt% NaCl brine system put forward few differences [12]. For  $\text{HLD} > 0$ , the catastrophic inversion line in formulation–composition map seems to be shifted to the left, i.e.  $A^+$  region has almost disappeared. It was previously shown that different parameters like surfactant concentration, stirring energy and phase's viscosity can affect the position of the vertical lines. In some extreme cases, such effect can reverse the stair shape. Concerning to the results obtained in this study, the first possible explanation for this behavior could be the viscosity of oil phase [14,15] which was 0.05 Pa s in this case. Few results [1,16] have shown that an increase of the oil phase viscosity displaces the upper vertical branch to the left for very viscous oil phases for which the stair may disappear or inverse. Indeed, this phenomenon can be explained by the fact that it is more difficult to make an emulsion where a very viscous phase is the continuous one. In other words, the more viscous phase tends to be dispersed in the less viscous one [17].

There are other cases where inversion line is similar to as shown in Fig. 2. For example, a system containing a mixture of anionic and non-ionic surfactants shows insensitivity to temperature, when temperature was varied as a formulation parameter [13]. For such cases it should be noted that the optimum temperature (systems exhibit three-phase behavior) should be different with each surfactant. The formulation–composition stair like maps for an anionic and a non-ionic surfactant are shown in Fig. 4. By combining a non-ionic surfactant with an anionic in certain ratio, it is possible to obtain a behavior such as plotted in Fig. 4c [13]. In this plot, the inversion line shifts from nearly horizontal (stair like maps) to nearly vertical.

Whatever is the reason for this typical formulation–composition map, now the aim was to understand if the positive and negative HLD has any significance over the characteristics of the emulsions and how emulsion's characteristics are influenced by a variation of composition especially in O/W region. Emulsions were characterized through microscopic images, average drop size and drop-size distribution, and rheology.

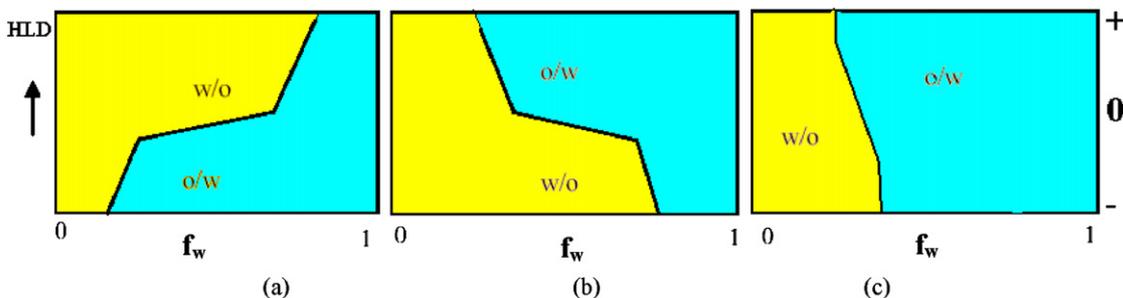


Fig. 4. A generalized formulation–composition map of an emulsion system with an emulsifier of type: (a) non-ionic (b) anionic and (c) mixture of anionic and non-ionic.

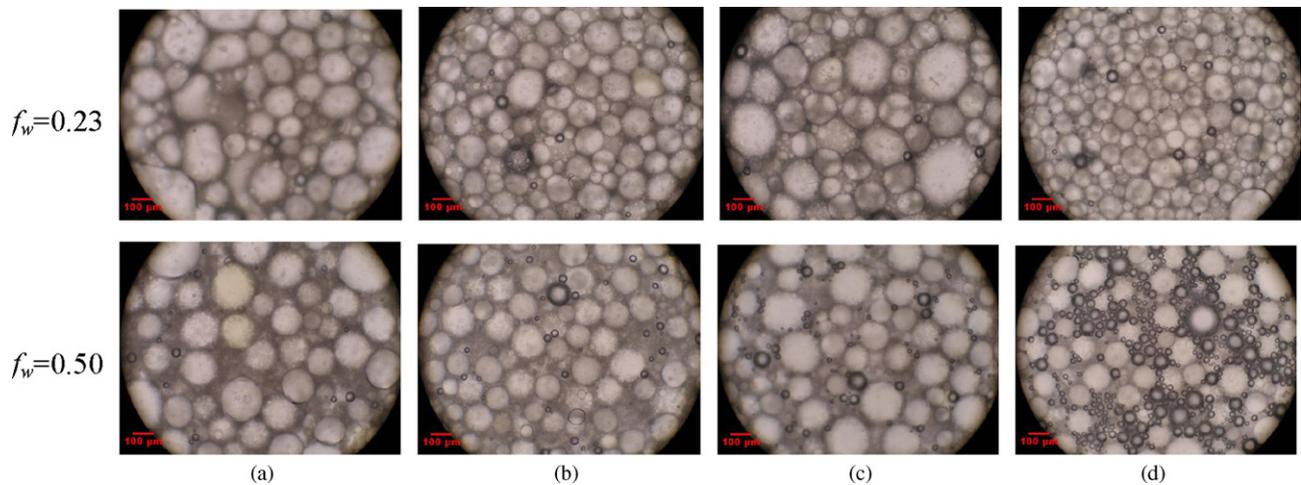


Fig. 5. Image of the droplets and their distribution in emulsions of  $f_w$  0.23 and 0.5 at different salt concentration (a) 1%, (b) 10%, (c) 15% and (d) 20% (w/v) and temperature 25 °C. Images were taken by an optical microscope.

### 3.2. Microscopic analysis of emulsions in formulation–composition map

The microscopic analysis of eight emulsions of different formulation–composition will be discussed. The conductivity measurement indicated that the emulsions on the left side of the inversion line had oil as a continuous phase. In the same zone, the microscopic images showed o/W/O multiple type of emulsions which were not stable. On the other hand, in the right side of the inversion line the emulsions were O/W type and they were comparatively stable. The degree of stability of emulsions at  $f_w$  0.23 was higher than  $f_w$  0.50 alike the other hydrocarbon-based emulsions. The images of the droplets at these  $f_w$  are compared in Fig. 5 in increasing order of salt. The distribution of droplets of corresponding emulsions is shown in Fig. 6.

The distribution of droplets at  $f_w$  0.23 was completely different from that of 0.5. For instance, at  $f_w$  0.5 a variation of salt concentration from 1 to 30% drastically modified the drop distribution (percentage volume of small droplets increased) and a significant decrease in average drop size. On the other hand, at  $f_w$  0.23 there were not much difference in population of smaller ( $30 \mu\text{m} > d > 2 \mu\text{m}$ ) or bigger ( $400 \mu\text{m} > d > 30 \mu\text{m}$ ) droplets except at salt concentration of 1 and 10%, where additional peaks at  $0.2 \mu\text{m}$  were observed. It should be noted that these two concentration of salt corresponds to  $\text{HLD} < 0$ . A careful observation of the images of droplets illustrates a special kind of small droplets which had a thick black outer surface. It can be a closed inter-bilayer of lecithin formed over oil droplets called as vesicles. Such vesicular structure is formed by lecithin when it exists in lamellar phase. The bilayers have the capacity to uptake water and swell. The population of such droplets was negligible at  $f_w$  0.23 irrespective of salt concentration, but at 0.5 their population increased significantly especially when salt concentration was increased from 15 to 20%. This could be the reason that the percentage volume of smaller droplets is higher than the bigger ones as seen in Fig. 5. The size of droplets and their distribution manifests the fluid behavior, i.e. rheology of an emulsion which is discussed in the following section.

### 3.3. Rheology of emulsions

Since emulsions had non-Newtonian behavior, it was difficult to characterize emulsions based on a unique viscosity value as used for Newtonian fluids. Since in process-equipments the shear rate is in the order of  $100 \text{ s}^{-1}$ , therefore viscosity of emul-

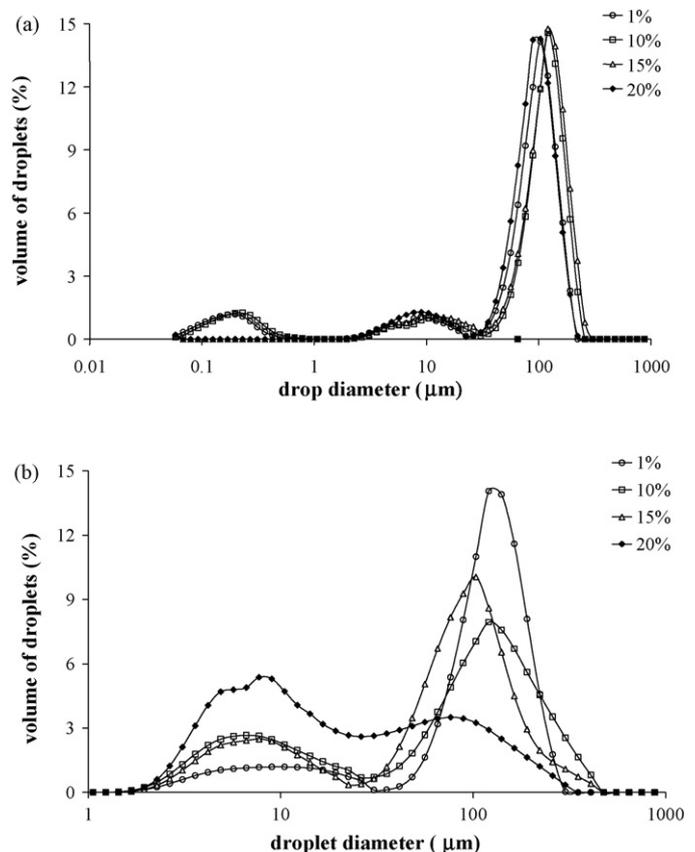


Fig. 6. Volume distribution of oil droplets in emulsions observed by particle size analyzer Mastersizer-MSS for (a)  $f_w = 0.23$  and (b)  $f_w = 0.5$  at different salt concentration (w/v). This measurement provided the average droplet diameter also as shown in Table 2.

Table 2  
Characteristics of emulsions obtained at 25 °C for different water fraction ( $f_w$ ) and at various salt concentrations

	Water fraction, $f_w$											
	0.23				0.5				0.79			
	1 <sup>a</sup>	10 <sup>a</sup>	15 <sup>a</sup>	20 <sup>a</sup>	1 <sup>a</sup>	10 <sup>a</sup>	15 <sup>a</sup>	20 <sup>a</sup>	1 <sup>a</sup>	10 <sup>a</sup>	15 <sup>a</sup>	20 <sup>a</sup>
$d_{43}$ ( $\mu\text{m}$ )	77	78	88	70	105	95	79	40	88	42	46	45
$\mu$ (Pa s) <sup>b</sup>	0.116	0.126	0.164	0.169	0.036	0.024	0.027	0.025	0.009	0.008	0.008	0.008

<sup>a</sup> Salt (%w/v).

<sup>b</sup> At  $\dot{\gamma} = 100 \text{ S}^{-1}$ .

sions was compared at this shear rate. At  $f_w$  0.23, viscosity of emulsion increased from 0.116 to 0.169 Pa s when salt concentration was increased from 1 to 20% (w/v). On the contrary, at  $f_w$  0.5 and 0.79, it remained constant. The difference in viscosity at these  $f_w$  was an order of magnitude. A comparison of viscosity with average drop diameter points out that the increase in viscosity with salt concentration is probably the result of colloidal interactions among the droplets and not the size of the droplets. This explanation applies to emulsions obtained at all  $f_w$ . It should be noted that the colloidal interactions depend very much on the inter-droplet distance and this distance decreases with decrease of water fraction. This can be the reason that colloidal interactions persist at  $f_w$  0.23 (and not much at 0.5 and 0.79) and hence it was influenced by salt concentration.

#### 3.4. Viscosity and drop size of emulsions over formulation–composition map

A formulation–composition map as shown in Fig. 2 is not a common type of formulation–composition map. This map is different from the usual in the manner of placing of the catastrophic inversion line in the region of  $\text{HLD} > 0$ . Therefore the deviation of emulsion's behavior from the normal one on a composition–formulation map should not be surprising. For example in low internal phase ratio 0.79 the type of emulsion was O/W even for  $\text{HLD} > 0$ , which is normally a multiple type w/O/W. The characteristics of emulsions at different formulation and composition are shown in Table 2. The experimental results show that the drop size does not vary much near the high internal phase ratio, i.e. at  $f_w$  0.23. The low-viscosity emulsions are found in the low internal phase ratio  $f_w$  0.5 and 0.79. These two facts are coherent with the normal formulation–composition map. On the other hand neither the viscosity nor the drop size behavior with respect to formulation shows the existence of transitional inversion line (i.e.  $\text{HLD} = 0$ ).

The above discussion was limited to direct emulsion formation, i.e. for a fixed composition and formulation during emulsion formation. There has been other way where formulation, composition or both are varied till phase inversion occurs during processing. Many authors have shown the hysteresis behavior with such method of emulsification and they have shown the shape of the hysteresis curve in positive and negative HLD zone. In the context of dynamic hysteresis, our further work will lead to the study of significance of positive and negative HLD on dynamic emulsification.

#### 4. Conclusions

The knowledge based on equilibrium phase behavior of lecithin permitted to put the emulsions on a unique formulation–composition map. In this work emulsions are prepared at various composition (water fraction) and formulation (salt concentration) to obtain the inversion line. It was found that the inversion line was not a common stair type rather than nearly a vertical line irrespective of HLD value. The catastrophic inversion line for positive HLD value in formulation–composition map seems to be shifted to the left, i.e.  $A^+$  region has almost disappeared. There are the cases where catastrophic inversion line has shifted right or left when a variation of surfactant concentration, stirring energy or viscosity of continuous or dispersed phases is in effect. For this study, the first two factors are identical for every combination of formulation–composition. Therefore, disappearance of  $A^+$  region can be related to the higher viscosity of sunflower oil [1] which was around 50 times of viscosity of aqueous phase at similar condition. The characteristics of few emulsions on composition–formulation map did not present any evidence of a phase inversion through formulation variable (salt concentration) except possibility of phase inversion through composition (water fraction). In addition, viscosity of oil-in-water emulsion seems to be the result of colloidal interactions which was modified with salt concentration rather than the size of oil-droplets especially at higher fraction of oil as an internal phase. The formulation–composition map of lecithin-based emulsion can be used to study the emulsification through dynamic phase inversion.

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