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Formulation–composition map of a lecithin-based emulsion

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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.

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 temperature (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 pharmaceutics, 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:

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

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

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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 (mS cm^{-1})
k_w	conductivity of aqueous phase (mS cm^{-1})
S	salt concentration in aqueous phase (%w/v)
t	constant depends on the type of emulsifier
ΔT	temperature difference with respect to 25 °C
x	volume fraction of sunflower oil in total volume of oil

Greek letters

α-EON	constant depends on the type of emulsifier
μ	viscosity of emulsion (Pa s)
$\dot{\gamma}$	shear rate (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 HLD = 0 is know as catastrophic inversion line, while the horizontal line (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.

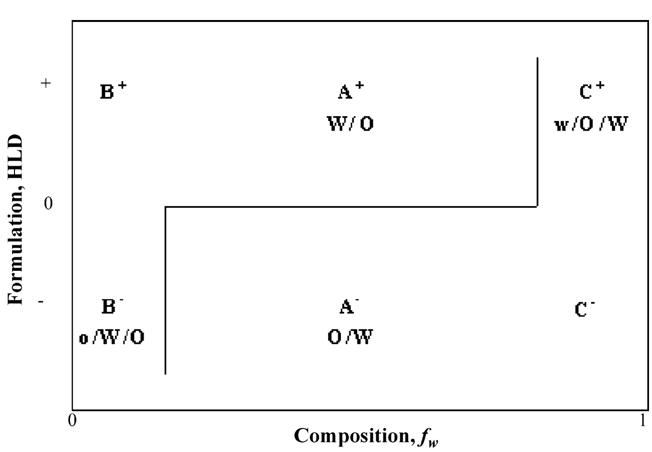

Fig. 1. A generalized formulation–composition map on two-dimensional plot [4].

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 follow (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