Food Research International 49 (2012) 672–676

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Short communication

Calorimetric studies of microemulsion systems with lecithin, isooctane and butanol

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ARTICLE INFO

Article history:
Received 24 May 2012
Accepted 21 August 2012

Keywords:
Microemulsion
Soybean lecithin
Enthalpy of mixing
Reverse micelles

ABSTRACT

In the present study, a thermodynamic analysis was performed using an isothermal titration microcalorimeter to measure changes in the enthalpy of mixing ($\Delta_{mix}H$) of water in microemulsion systems formed by soybean lecithin, isooctane and butanol. These energies were important to determine the driving forces associated with the formation of reverse micelles. It was observed that the titration curves of water in pure isooctane and in isooctane with soybean lecithin present values of $\Delta_{mix}H$ equal to -9.46×10^{-3} kJ/mol and -5.68×10^{-3} kJ/mol, respectively. This shows that water does not form intermolecular interactions with these components. Exothermic behavior, with values of $\Delta_{mix}H$ ranging from $+2.17$ kJ/mol to -1.63×10^{-2} kJ/mol, was observed from the titration curve of water in systems formed by soybean lecithin, isooctane and butanol. These values were associated with the water dissolution process, where the formation of reverse micelles had been observed in the evaluated systems. Differences in behavior of $\Delta_{mix}H$ for the water curves were observed in systems formed by butanol and soybean lecithin, only pure butanol and butanol with isooctane. The curve of the system containing soybean lecithin, butanol and isooctane clearly shows that the formation of aggregates occurred in this system (reverse micelles). Finally, it was also noted that soybean lecithin did not suffer any degradation process, since the energy involved in the process of water titration in the systems containing the same substance was considered low. Thus, soybean lecithin may be used without problems in this type of system.

1. Introduction

Over the past decades microemulsions have been widely studied, mainly due to their potential applications in diverse fields including preparation of nanoparticles with electrochemical and catalytic properties, separation of water-soluble and lipid soluble substances, fat-soluble vitamins and other lipid compounds by electrokinetic chromatography or liquid chromatography, enhanced oil recovery, liquid–liquid extraction, removal of contaminants from solid surfaces and capillaries from tissues in the pharmaceutical and cosmetic industries (Hellweg, 2002). The growing interest in microemulsions for cosmetic and pharmaceutical applications has been linked to its physical properties of thermodynamic stability, spontaneous formation, clear appearance, low viscosity and high solubilization capacity (Malmsten, 2002; Schmidts et al., 2009).

Microemulsions are composed of water–oil-surfactant and sometimes alcohol as a co-surfactant. These systems have been the subject of extensive research in recent decades, mainly due to their high solvent potential (Solla-Gullón, Rodes, Montiel, Aldaz, & Clavilier, 2003; Patel, Schmid, & Lawrence, 2006).

The use of alcohol as a co-solvent in the preparation of microemulsions has a long history. Alcohol is added to ionic surfactants to compensate the salting-out effect, reducing the interaction of proteins with water caused by the solvation of ions in saline solutions. This effect is demonstrated by a mild turbidity of the solution. In the case of nonionic surfactants, the alcohol typically plays the role of balancing interactions of this surfactant with water and the organic solvent, thus decreasing the interfacial tension between oil and water phases which is often elevated by the commercial surfactants (Gradzielski, 1998). Alcohol can change the spontaneous curvature of the surfactant film when its penetration into the interface is sufficient to increase the flexibility of the interface (alcohol as

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http://dx.doi.org/10.1016/j.foodres.2012.08.014

co-surfactant), or it can change the polarity of the polar and nonpolar phases (alcohol as a co-solvent) (Shevachman, Shani, & Garti, 2004).

Lecithin (phosphatidylcholine) is a natural phospholipid found in the composition of most organisms, accounting for more than 50% of the lipid matrix of biological membranes. The behavior of lecithin in water and organic solvents is of great interest for several reasons. Because lecithin is viewed as a fully biocompatible substance, it is widely used in many areas as a surfactant for systems in which water and oils are used in food and feed, medicines, cosmetics and pharmaceutical products (Angelico et al., 2004).

Several studies have been performed on soybean lecithin microemulsions due to the formation of nontoxic microemulsions (Papadimitriou et al., 2008). The workgroup of Angelico et al. has conducted numerous studies using soybean lecithin microemulsions in different organic solvents such as isooctane, decane, cyclohexane and others, mainly for evaluating the phase behavior of such systems (Angelico et al., 1998, 1999, 2000, 2002, 2004). Investigation of the phase behavior of soybean lecithin microemulsions composed of triacylglycerol and water with different types of alcohol was performed by Leser et al. (1996). It is observed that alcohol acts as a co-solvent in the formation of reverse micelles in the evaluated systems. Caboi et al. (2005) evaluated the use of butanol in systems composed of lecithin, tripalmitin, water and oil, verifying the fact that the presence of butanol promotes the formation of a vast isotropic liquid phase in the phase diagram of this system, indicating that butanol helped to stabilize this system by acting as a co-surfactant in the formation of reverse micelles.

Despite the fact that soybean lecithin is widely used in the stabilization of mixtures of water and edible oils, formulation of drugs and cosmetics (Corswant, Thor´En, & Engstrom, 1998), and extraction of biomolecules using reverse micelles (Hasmann, Gurpilhares, Roberto, & Pessoa, 2007) the calorimetric thermodynamic study of systems containing soybean lecithin, water, organic solvent (isooctane) and alcohol (butanol), in order to evaluate the energy of the reaction involved in the process of micelle formation of such a system, has not been performed. Therefore, the aim of this study was to determine the amount of energy involved in the micelle formation process of soybean lecithin in systems with water, isooctane and butanol, using the isothermal titration microcalorimetric (ITC) technique.

2. Materials and methods

2.1. Materials

Soybean lecithin was purchased from *Cargill Brazil* (Sao Paulo—Brazil) with 85% of purity (phosphatidylcholine), 8% of phosphatidylethanolamine, 6% carbohydrates and 1% moisture. The solvents isooctane and butanol were purchased from *Vetec Quimica Fina* (Rio de Janeiro—Brazil). All reagents used were of analytical grade.

2.2. Measurement of turbidimetric titration

One milliliter of a solution containing soybean lecithin, isooctane and butanol was placed in a 4 mL tube that was maintained at a temperature of 25 °C. Soybean lecithin concentrations varied from 1.00 to 20.00% (w/w). The solvent concentrations were fixed in relation to each other at 70.00% (w/w) of isooctane and 25.00% (w/w) for butanol. To this solution 2 μL aliquots of distilled water were continuously added until the appearance of turbidity in the resulting solution. This system was left at rest (15 to 30 min) until the appearance of two clear phases. The amount of water added to each system to cause the appearance of two phases was registered. This procedure was repeated for each tube containing the system with increasing concentrations of lecithin in isooctane and butanol, totaling to 20 tubes at the end of the experiment. From the values of the amount of water solubilized in each system it was possible to obtain a solubility curve for water in solutions containing soybean lecithin (1.00 to 20.00% w/w) in isooctane and butanol.

2.3. Microcalorimetric study of the system

Measurements of the changes in enthalpy of mixing, $\Delta_{mix}H$, were obtained using an Isothermal Titration Microcalorimeter (CRC, Model ITC 4200, USA). The microcalorimeter consists of a pair of cells with a capacity of approximately 1.8 mL; into which one of them, the reaction cell, the sample to be titrated was placed, while the other cell contained a reference sample. Surrounding these cells is a system of thermopiles sensitive to small energy fluxes in the form of heat. A syringe was used to add 1 μL of water at 3600 s intervals into the reaction cell. At the same time, the solution was stirred at 300 rpm and at a temperature of 25 °C. The experiment was divided into six thermodynamic cycles, with the molecular relationship among the components always equal to that used in the first cycle. The first cycle consisted of a system containing soybean lecithin (5.00% w/w) in isooctane (70.00% w/w) and butanol (25.00% w/w). In the second cycle, soybean lecithin + isooctane was used, while in the third cycle the reaction cell was filled with lecithin + butanol. In the forth cycle, the system used was composed of butanol + isooctane. In the fifth cycle, the reaction cell was filled with pure isooctane. Finally, in the last cycle, pure butanol was used and titrated with water.

Each measurement of energy flow creates a peak that represents the change in energy associated with the injection of a small volume of water to the analyzed system (Fig. 1). As the analyzed system reaches saturation, the released energy signal decreases until it reaches full saturation. By integrating the area of each peak (energy released over a period of time) the measurement of ΔH is obtained (in units of joules per mole of water) from the reaction of water with the components of each evaluated system.

3. Results and discussion

3.1. Diagram of water solubility in the ternary system composed of soybean lecithin–isooctane–butanol

The addition of water in pure isooctane or isooctane with soybean lecithin produces a biphasic system in which even small amounts of water (1 μL) is separated from the organic solvent, regardless of the presence of soybean lecithin. However, the presence of butanol results in increased miscibility of water in the ternary system. Results of the measurements of water solubility in the system formed by isooctane 70.00% (w/w)/butanol 25.00% (w/w) with different concentrations of soybean lecithin are shown in Fig. 2.

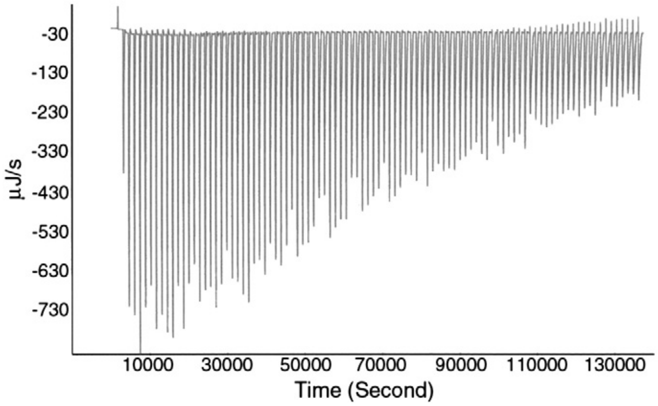

Fig. 1. Deflections corresponding to the change of power by making consecutive injections of water in isooctane/soybean lecithin/butanol.