

PH EFFECT ON VISCOELASTIC BEHAVIOR AND PHYSIOCHEMICAL PROPERTIES OF WALNUT OIL EMULSIONS

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ABSTRACT:

The influence of pH of walnut oil emulsions on droplet morphology, droplet size distribution, time and temperature stability, and rheological properties has been studied. It has been found that walnut oil based emulsions form a metastable gel-like microstructure at steady conditions revealed by a linear viscoelastic response at low deformations. Flow curves of investigated emulsions demonstrated shear thinning behavior at moderate shear rates with a tendency to a limiting viscosity at higher loads. The most stable emulsion was formed at weakly acidic conditions (pH = 6), which favors the formation of fine uniform droplets with no visible tendency to coagulation at ambient conditions.

KEY WORDS:

emulsion stability, viscoelasticity, viscosity, shear thinning, pH effect, droplet morphology

1 INTRODUCTION

Emulsions usually consisting of two or more liquid immiscible phases are thermodynamically unstable systems prone to phase separation driven by tendency to minimization of the interfacial area between the aqueous and the oil phase. Since many years they are among the most important colloids in numerous applications in the food, cosmetics and pharmaceutical industries [1, 2]. In many cases the emulsion contains also a surface active agent, which has two main functions: the first one is to decrease the interfacial tension between phases; thereby enabling easier formation of the emulsion; and the second one is stabilization of the dispersed phase against coalescence once it is formed. Emulsions can be classified into two broad groups: simple emulsions and multiple emulsions. In the case of simple emulsions, droplets of one liquid phase are dispersed in another immiscible continuous phase [2]. Beside such emulsions there are double emulsions described as "emulsions of emulsions" [3]. For example, an oil-in-water-in-oil (O/W/O₁) double emulsion consists of small oil (O) droplets dispersed in aqueous phase (W) and this O/W emulsion itself is dispersed as large droplets in the continuous oil phase (O₁). In the case of a water-in-oil-in-water (W/O/W₂) double emulsion, an emulsion of small water (W) droplets in oil

(O) is itself dispersed as large droplets in the continuous aqueous (W₂) phase [3].

Emulsions are metastable systems and their initial structure evolves with time during storage and/or transportation as a result of thermal treatments, mechanical stresses, physical coarsening and biological action [4]. Thus, the main challenge raised by the application of emulsions is their thermodynamic instability. Indeed, they are prone to destabilization and phase separation. During emulsification, the interfacial area between the continuous and the dispersed phases is considerably augmented compared to the interface before homogenization. The interfacial free energy is therefore significantly increased. According to thermodynamics all the metastable systems develop to attain their minimum energy state, which in the case of emulsions is manifested by a great tendency to phase separation in order to minimize the interfacial contact area and free energy. This instability manifests itself by various mechanisms: flocculation, coalescence, creaming or sedimentation, and Ostwald ripening [5]. Emulsion stability and rheological behavior is related to several factors such as volume fraction and viscosity of the dispersed phase, droplet granulometry, viscosity of the continuous phase as well as its chemical composition (polarity, pH), nature and electrolyte concentration, and interfacial rheology.

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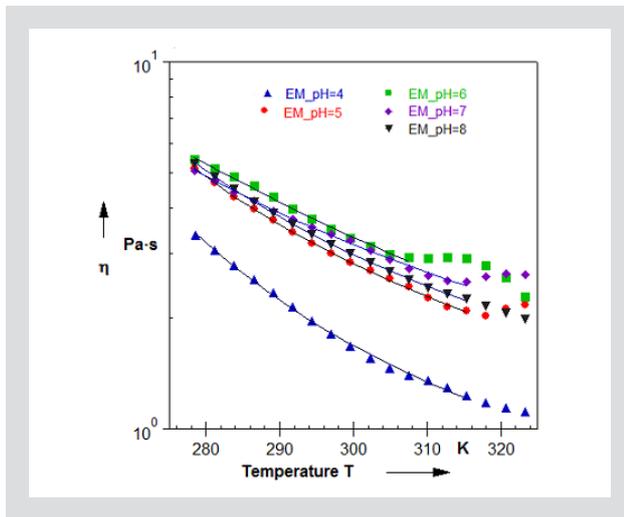


Figure 7: Influence of temperature on the apparent viscosity (at 100 1/s) for emulsions of different pH. Arrhenius fits are shown as solid lines.

sions with pH 4 and 8 is similar with no significant coalescence within the measured temperature range. The rest of materials were less stable against temperature as may be deduced from Figure 6 and from the values shown in Table 4.

In emulsions of pH = 5, 6, and 7 droplet coalescence, evidenced by a characteristic minimum on a viscosity curve, was induced under the experimental shear conditions above 35–40 °C. After this minimum an increase of viscosity with temperature was noticed. Similar atypical thermal behavior was observed previously in oil in water emulsions stabilized with sucrose palmitate [18]. The authors attributed an increase in viscosity at elevated temperatures to the shear induced droplets deformation and breakdown, which takes place in concentrated emulsions and in consequence may led to droplet bursting or irreversible coalescence. Other possible explanation is shear induced droplet size redistribution coming from breaking of droplets at elevated temperature due to interfacial tension gradients [24].

4 SUMMARY

The applied preparation procedure allowed for formation of stable emulsions of walnut oil in water. Average particle size of all the systems found between 2.81–3.58 microns and the values of dispersity indexes close to unity (1.00–1.23) confirm sufficient stability at ambient conditions without visible phase separation or droplets disruption. Microscopic observations showed however the presence of small amounts of bigger droplets in emulsions of pH = 4, 5 and 8, which may initiate the droplet coalescence and accelerate emulsion degradation. Among the prepared emulsions, that of pH = 6 was the most stable as confirmed also by rheological tests. In general the emulsions of fine droplets with uniform size distribution exhibited higher viscosities and better long term stability than those of higher dispersity

index. Oscillatory tests revealed the formation of weak gel-like microstructure at steady conditions characterized by linear viscoelastic behavior at low deformations. The stability of our materials was demonstrated also by domination of storage modulus G' over loss modulus G'' through the wide frequency range and small slope of G' at low frequencies. It has been found also that pH affects the emulsions stability at elevated temperatures. The acidic and basic emulsions (pH = 4 and 8) showed no coalescence during shearing at 100 1/s within the temperature range 20–60 °C. In emulsions of pH = 5, 6, and 7 the appearance of a characteristic minimum on an apparent viscosity curve indicated thermally induced droplet disruption followed by emulsion degradation.

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