Colloids and Surfaces A: Physicochem. Eng. Aspects 494 (2016) 81–86

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

An Ouzo emulsion of toluene in water characterized by NMR diffusometry and static multiple light scattering

Ali Reza Tehrani-Bagha [a], Aina Viladot [b], Krister Holmberg [b], Lars Nordstierna [b,*]

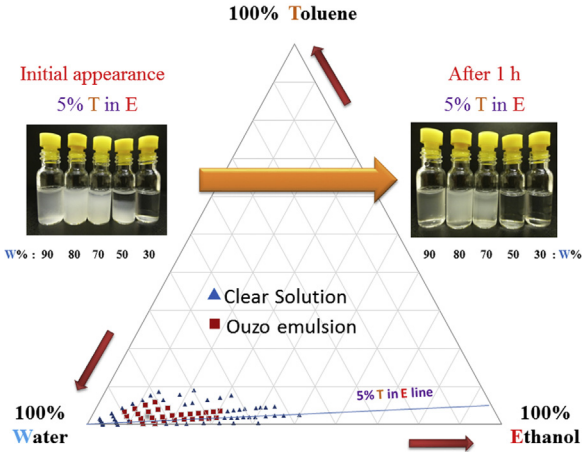
[a] Department of Chemical and Petroleum Engineering, Faculty of Engineering and Architecture, American University of Beirut (AUB), Beirut 1107 2020, Lebanon

[b] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

HIGHLIGHTS

- Bimodal droplet size distribution in toluene/ethanol/water Ouzo emulsions.
- Complementary methods by NMR diffusometry and light scattering.
- Spectrometrically time-resolved phase separation study of the Ouzo emulsion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form 5 January 2016
Accepted 7 January 2016
Available online 12 January 2016

Keywords:
Ouzo emulsion
Spontaneous emulsification
NMR diffusometry
Multiple light scattering
Emulsion stability

ABSTRACT

An Ouzo emulsion is an emulsion that is formed spontaneously by adding water to a system comprising a hydrophobic substance (like anethole in the Ouzo beverage), a water-miscible solvent and (optionally) water. Formation of such an emulsion does not require the use of surfactants, dispersing agents, or mechanical agitation. In this work, Ouzo emulsions were prepared from the ternary mixture toluene–ethanol–water and the emulsion stability was studied by a combination of two techniques: static multiple light scattering and NMR diffusometry. A bimodal distribution of the droplets was found. The light scattering technique revealed the presence of large drops, several micrometer in size. NMR measurements confirmed the large drops but also showed the additional presence of droplets of the order of 100 nm in diameter. The distribution of toluene between the three environments (i) large drops, (ii) small droplets, and (iii) the continuous ethanol–water phase could also be assessed. It was found that addition of an anionic surfactant to the system yielded an improved dispersed system, i.e., more toluene was present as small droplets and less toluene was dissolved in the ethanol–water phase; however the presence of the amphiphile reduced the emulsion stability.

* Corresponding author. Fax: +46 31 16 00 62.
E-mail address: lars.nordstierna@chalmers.se (L. Nordstierna).

http://dx.doi.org/10.1016/j.colsurfa.2016.01.008
0927-7757/

1. Introduction

An 'Ouzo emulsion' is an emulsion that has been created according to the same principle as applies to the famous Greek aperitif [1–3]. The Ouzo that is sold in bottles is a clear and colorless alcoholic liquid. When ice water is added to a glass of Ouzo, the mixture becomes turbid due to formation of an emulsion. The emulsification is spontaneous and the liquid remains turbid for a long time, i.e., the phase separation is slow. Ouzo is not the only drink that shows this behavior; the French aperitif 'Pernod' and the Turkish beverage 'Raki' are other well-known examples.

Ouzo and similar beverages are produced from extracts that are derived either from distillation in the presence of anise seeds or from extracting the seeds in ethanol [1]. The main component of anise is anethole, a phenylpropene derivative. Anethole is highly soluble in ethanol but its water solubility is very low. The ethanol content in the commercial beverage, around 40%, is enough to keep anethole in solution but once water is added the solubility limit is exceeded and anethole separates out as an emulsion [4]. The anethole droplets are likely to be stabilized by polar lipids and other amphiphilic substances from the flavoring agents added in the production process.

Ouzo emulsion is the result of a spontaneous emulsification between two immiscible components in the presence of a third component in which both components are soluble. For preparation of an Ouzo emulsion, generally a hydrophobic liquid (e.g., anethole) is dissolved in a water-miscible solvent such as ethanol. An excess of water is then added under gentle stirring to the mixture. The hydrophobic component will not be soluble in the solvent mixture but will form oil nuclei in the solution. These nuclei will grow in size and eventually reach a diameter large enough to give a milky appearance [5]. Such emulsions often have a very uniform droplet size, which indicates that the droplets are formed by homogenous nucleation. The reported mean droplet diameter measured by small angle neutron scattering, dynamic light scattering and particle size analyzer, was in the range of 0.8–4 μm [3,4,6]. It is important to note that the emulsification proceeds spontaneously. The stirring is there to make the formation of oil nuclei a uniform process, not to disintegrate an oil phase. A limitation of the process is that it only gives very dilute oil-in-water emulsions; nevertheless, the Ouzo procedure is of interest for making emulsions for pharmaceutical and cosmetic applications (e.g., drug delivery) [7].

We have been interested in the Ouzo procedure and in the present paper we report on an investigation of the size of the droplets formed when water is added to a solution of toluene in ethanol. Different ratios of the three components were used and two complementary techniques, NMR diffusometry and a static multiple light scattering technique, were employed for droplet size determination. NMR has previously been used for studies of the Ouzo procedure. Carteau et al. used DOSY (diffusion ordered spectroscopy) and TOCSY (total correlation spectroscopy) experiments to monitor the emulsification in the anethole–water–ethanol system [5,8,9]. The studies supported the view of formation of small nuclei of a few nanometers in diameter, which subsequently underwent coalescence into larger drops. Light scattering has also been used previously to study Ouzo emulsions. Based on results from a dynamic light scattering study, Sitnikova et al. reported that the droplet growth was governed by Ostwald ripening and by the volume fraction of the dispersed phase [6] and these findings were in accordance with reported results from neutron scattering experiments [4]. Evidently, the NMR techniques and the scattering experiments applied to the same system (anethole–water–ethanol) have resulted in somewhat diverging observations. One objective of the present investigation was to shed light on this somewhat unclear situation by employing in one study both NMR diffusometry and a scattering technique on a model Ouzo system.

2. Materials and methods

2.1. Materials

Reagent grade toluene and ethanol (purity >99.8%) were purchased from Sigma–Aldrich and Kemetyl, respectively. Millipore water (resistivity ~18 MΩ) was used for emulsion preparation. Deuterium oxide (99.8 atom% D) was purchased from Dr. Glaser AG (Basel, Switzerland) and used for the NMR measurements.

2.2. Emulsion preparation

Various mixtures of toluene, ethanol and water were prepared by adding water to solutions of toluene in ethanol with known concentrations (1, 5, 10, 20, 30, and 40 wt.% respectively). The systems that were stable for more than 1 h were regarded as proper Ouzo emulsions in order to specify the Ouzo emulsion region on the ternary phase diagram. Further investigations were performed by light scattering and NMR diffusometry on a few selected compositions from this region. It should be noted that for the NMR measurement, D_2O was used instead of H_2O for preparation of the Ouzo emulsions.

2.3. Experimental techniques

2.3.1. Light scattering

A static multiple light scattering device with near infrared radiation (TurbiScan™ MA 2000) from Formulactions (France) was used for monitoring the stability of emulsions in real-time. This is an optical instrument designed to study the processes of aggregation and phase separation in colloidal systems. The device works with a pulsed near infrared light source (λ = 880 nm) and two synchronous detectors for transmission (at 180°) and backscattering (at 45°) that move up and down along a cylindrical glass cell containing the sample [10]. The measured backscattered and transmitted light fluxes depend on the mean path of photons in the dispersion. These physical parameters, which depend on particle diameter and volume fraction, give information on the state of the dispersion.

The Ouzo emulsions were prepared in glass vials and monitored by the Turbiscan instrument every 20 min for 24 h. The stability of the emulsions can be compared based on the migration velocity obtained from the changes in transmission profiles by time.

The quantitative analysis of the droplet size diameter of the emulsions was calculated based on the modified Stoke's equation given by Eqs. (1) and (2), which are described in detail elsewhere [11]. By obtaining the particle migration velocity from the measurements and knowing the density and viscosity of the dispersed and continuous phases [12], one can calculate the mean diameter $\langle D \rangle$ of the dispersed droplets in the emulsion from the following equation:

$$\langle D \rangle = \sqrt{\frac{18\eta V Q}{(\rho_C - \rho_D) g}} \quad (1)$$

where η is the viscosity of continuous phase, ρ_C and ρ_D are the density of the continuous and dispersed phases, respectively, g is the acceleration due to gravity (9.8 m/s^2), V is the migration velocity which is obtained from the light scattering measurements, and Q is the correction factor for the concentrated dispersions. The latter can be obtained from the following equation:

$$Q = \frac{1+(4.6\varphi/(1-\varphi)^3)}{1-\varphi} \quad (2)$$