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Liquid Droplet Dispersions Formed by Homogeneous Liquid−Liquid Nucleation: "The Ouzo Effect"

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The "ouzo effect" enables one to create a dispersion of small droplets in a surrounding liquid phase without the use of surfactants, dispersing agents, or mechanical agitation: a phenomenon which can be of value in many disciplines. In the quantitative studies presented here, dispersions of oil droplets in water are formed by the addition of water to a solution of the oil dissolved in a solvent. This causes the oil to supersaturate and then nucleate into small droplets. The mean droplet diameter is a function only of the oil-to-solvent ratio at a given temperature. The number density of droplets formed can be controlled independently from the droplet diameter by changing the amount of water added. Smaller droplets are formed by using more hydrophilic cosolvents. The droplet size distribution is typically log−normal. The width of the distribution can be narrowed by mixing the components at an elevated temperature and then allowing the dispersion to cool.

1. Introduction

When water is added to ouzo, an alcoholic beverage common in Greece and other Mediterranean countries, the anise oil dissolved in the ouzo spontaneously nucleates into many small droplets. These small droplets scatter light, causing the drink to appear milky white. This effect is a basic physical phenomenon which occurs in liquid systems involving three or more components. The simplest case to study is a ternary liquid system, such as the ouzo example. When water is added to a dilute binary solution of a solute whose solubility in water is very small (e.g., anise oil) in a solvent (e.g., ethanol), most of the solute will rapidly come out of solution. For certain proportions of solute, solvent, and water, a relatively stable dispersion of very small solute droplets is formed. Note that the third component need not be water; any substance which is miscible with the solvent but not the solute will produce a two-phase dispersion. The authors have termed this process of creating metastable liquid−liquid dispersions "the ouzo effect".

There have been numerous previous studies by other researchers on the formation of droplet dispersions, several of which are discussed below. The phenomenon presented here is distinct from those of other publications on droplet dispersions, because the ouzo effect allows one to create relatively stable droplet dispersions, without the use of surfactants, stabilizers, or any form of mechanical agitation. The authors will show that the mean droplet size, size distribution, and number density are controllable (over a limited range) by varying the proportions of the three components, their densities, their mutual solubility, and the temperature. The trends in droplet size, distribution, and number density are explained qualitatively on the basis of the fact that the droplets are formed by homogeneous liquid−liquid nucleation.

2. Background of the Ouzo Effect

Figure 1 is a right triangle, three-component, phase diagram which shows the concentration of a solute on the

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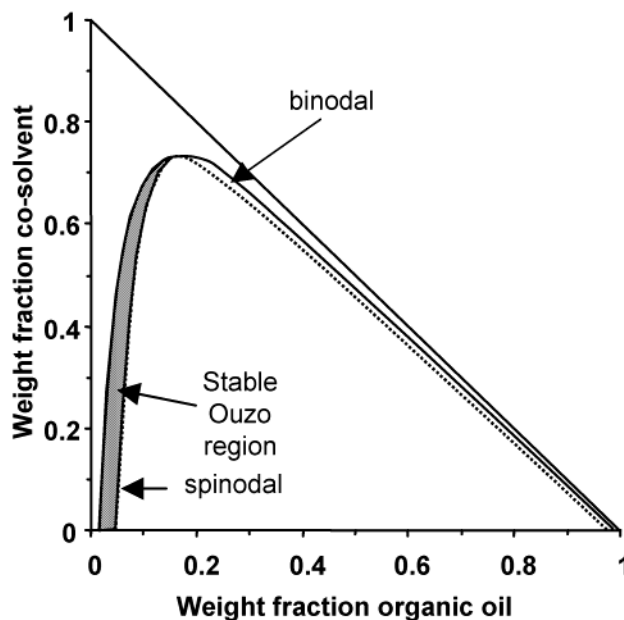[†] E-mail: jlk@jhu.edu.

Figure 1. Right triangle three-component phase diagram at constant temperature and pressure. The ouzo effect occurs for solutions brought from the one-phase region into the metastable region between the binodal and spinodal curves.

abscissa and the concentration of a solvent on the ordinate. The concentration of the third component (e.g., water) is found by difference. On this diagram, one can trace out the binodal (or miscibility-limit curve) and the spinodal (or stability-limit curve). The binodal on a phase diagram traces the thermodynamic minima in the Gibbs free energy of a system as a function of temperature or of mole fraction. The spinodal traces the limit of thermodynamic stability. It is possible for a system to exist for a very long time in states between the spinodal and the binodal, that is, a "state" for which the Gibbs free energy is not minimized, if there are large kinetic barriers to the phase separation. The set of all such nonequilibrium but very long-lived "states" is called "the metastable region". Superheated liquids are a common example of single component systems in this state. If a single-phase multicomponent solution existing in the metastable region is sufficiently perturbed,

the solution will spontaneously separate into two phases, the compositions of each of which will be on the binodal curve. The supersaturation of a solution is (approximately) the ratio of the actual concentration of solute to the concentration of solute at the binodal.

The ouzo effect occurs when solutions are rapidly brought sufficiently into the metastable region by the addition of water. When the solubility of some of the solutes decreases more rapidly than linearly with increasing water concentration, the solution can become supersaturated in these components. If the supersaturation is large, nuclei form spontaneously from small local fluctuations in concentration of solute molecules. This process is known as homogeneous nucleation. The nuclei have a larger than average concentration of solute; thus, their formation causes a depletion of solute near each nucleus. As a result, further nucleation occurs *only* in the as yet depleted regions, as far as possible from existing nuclei. Nucleation ends when there remain no regions with a high supersaturation. The end result of this process (which occurs on the millisecond or faster time scale) is a spatially, fairly uniform dispersion of very small liquid droplets suspended in the continuous liquid phase. Further growth of the droplets occurs almost entirely by Ostwald ripening, wherein the smallest droplets dissolve, since the concentration has dropped to below the saturation concentration for droplets of their size, and the larger ones grow, since their saturation concentration is smaller. This process occurs very slowly (seconds and longer), since the net dissolution rates are very small and the diffusion rates of the molecules become small as the droplets become fewer and thus farther from each other.

It should be stressed that the ouzo effect is not spinodal decomposition. If a system which is initially in the one-phase region of the diagram is quickly brought inside the spinodal curve by changing its composition, the one-phase solution will rapidly separate into two phases. Inside the spinodal, the system is unstable to long wavelength concentration fluctuations. The longest wavelength fluctuations grow rapidly in amplitude,[1] resulting in large droplets which appear to suddenly pop out of solution (millisecond timescale). Two novel liquid−liquid extraction processes based on spinodal decomposition, called composition induced phase separation[2] (CIPS) and temperature induced phase separation[3] (TIPS), recently have been proposed.

The ouzo effect and the CIPS processes have different useful applications. In the CIPS process, spinodal decomposition causes the extremely rapid formation of large droplets. These large droplets rise or fall very rapidly in the solution; thus, a bulk continuous second phase is quickly formed.[4] The CIPS process is useful when one desires rapid phase separation *without* emulsion formation, as in liquid−liquid extraction. The ouzo effect is due to homogeneous nucleation, so the droplets initially created are extremely small. Since the initial rate of nucleation is extremely large, so many droplets are formed that further growth occurs very slowly. As a result, the ouzo effect is useful when one wishes to create long-lived micron-sized droplets without the use of mechanical agitation.

It also should be noted that oil-in-water dispersions similar to those of interest in this study have been studied previously under the headings of spontaneous emulsification and microemulsion formation,[5−12] but these are not the same phenomena as the ouzo effect. When two immiscible liquid phases are brought into contact, it is sometimes observed that small droplets of one component are spontaneously formed near the interface in one or both of the continuous phases. It has been proposed that slow diffusion of one solution into the other results in "stranding" of a particular insoluble component, which then aggregates into droplets.[5,12] An explanation[1,2] for microemulsion formation is that it occurs when concentrations are such that the interfacial tension between the two (to be formed) phases is extremely small (<10 dyn/cm). Then, the entropy of mixing is large enough to make the phase separated system the stable one. In common solutions, the entropy of mixing is completely negligible. In both of these cases, droplet dispersions are formed slowly from the contact of two immiscible continuous liquid phases. The ouzo effect, on the other hand, is a very rapid process which produces droplet dispersions without contacting two bulk immiscible liquid phases.

To the authors' knowledge, there have been only two publications which have analyzed or utilized the ouzo effect. Ruschak and Miller experimentally and theoretically studied the ethanol−toluene−water system,[7] in both the ouzo effect and the spinodal decomposition regions. McCracken and Datyner[13] reported a novel method of "true emulsion polymerization" in which water is added to a styrene−methanol solution. The micron-sized styrene droplets then were polymerized to form a latex of small polystyrene beads. This "true emulsion" is another example of the ouzo effect. Polymerization of droplets produced by the ouzo effect may become useful for a number of practical applications, such as polymer beads for microencapsulation of pharmaceuticals, or for producing tracer particles[14,15] for particle displacement velocimetry studies.

3. Experimental Details

In this work, water always is used as the third component. The solute/solvent solution becomes increasingly supersaturated as more and more water is added; droplets are formed when the supersaturation of the solute becomes high enough (see Figure 1). To prevent confusion, the term "ratio" will be used when referring to the concentration of organic solute in the solvent *before* the addition of water, and "weight percent" will be used for the concentration of solvent in the two-phase dispersion *after* the addition of water.

Several different water-insoluble organics were used to produce the ouzo effect: divinyl benzene (DVB), *N,N*-dimethylaniline, fluorotoluene, fluorostyrene, and benzyl alcohol. Three different water-miscible solvents for the oil were used: ethanol, DMSO,

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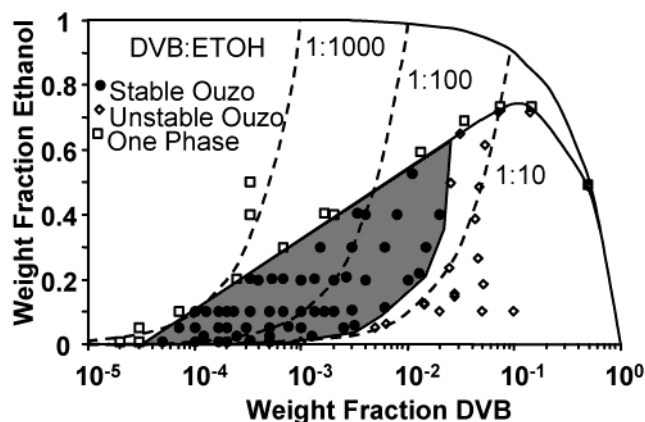(15) Dong, R.; Chu, S.; Katz, J. *J. Fluids Eng.* **1992**, *114*, 393−403.

Figure 2. Right triangle phase diagram showing the region (indicated by heavy shading) in which the ouzo effect occurs for the DVB–ethanol–water system at room temperature. Solid circles are experimental points where stable dispersions of small DVB droplets were observed, open diamonds indicate where very large droplets or two continuous phases were observed, and open squares show where a single phase was observed.

and acetonitrile. All chemicals were obtained from Aldrich. The DVB was prepared by washing repeatedly with a sodium hydroxide solution to remove the polymerization inhibitor *tert*-butylcatechol and other impurities. The DVB was then dried, and both the DVB and water were filtered through a 0.22 μm filter. The other chemicals were used as received.

To create the ouzo effect, a small measured quantity of DVB (for example) was added to a quantity of ethanol to make a solution of the desired oil-to-solvent ratio. The solution was agitated slightly until a clear, single-phase solution was formed. Water was then added to the solution to dilute the ethanol to the desired weight fraction, resulting in the supersaturation of the DVB and the nucleation of small droplets. The result was a milky white dispersion of droplets throughout the continuous water–ethanol phase. Note that the water was added by rapidly pouring a measured quantity into a 20 mL glass vial containing the DVB–ethanol solution. The resulting droplet dispersion was not intentionally mixed or agitated, since it was observed that agitation would cause shearing and breakup of the larger droplets formed by homogeneous nucleation.

The size distributions of the droplets in the dispersion were obtained using an Elzone PC-112 particle size analyzer. This instrument operates by pumping a sample of the dispersion through a 30 μm orifice and measuring the change in electrical resistance across the orifice as a droplet passes through. The change in resistance is proportional to the droplet volume. The particle size analyzer produces a histogram of the size distribution of the droplets counted.

4. Results

A. Stable Ouzo Region. The ouzo effect takes place in the metastable region of the ternary oil–solvent–water phase diagram. In Figure 2, the one- and two-phase regions of the three-component DVB–ethanol–water system are shown on a right triangle diagram. This figure is similar to Figure 1 except that, for the weight fraction of DVB, a logarithmic scale was used, thus enabling very small concentrations of DVB to be shown. The ouzo effect occurs only in the portion of the phase diagram where the oil is dilute because the DVB is very insoluble in water. As expected, the ouzo effect occurs in the metastable region of the phase diagram, between the spinodal and the miscibility limit, that is, the binodal. Within this region, labeled "stable ouzo region" and indicated by heavy shading in Figure 2, the oil nucleates into small, stable droplets upon the addition of water. At 23 °C, the solubility of DVB in water is 3×10^{-5} weight fraction and increases with increasing weight fraction of ethanol. The solid line in Figure 2 represents the experimentally determined
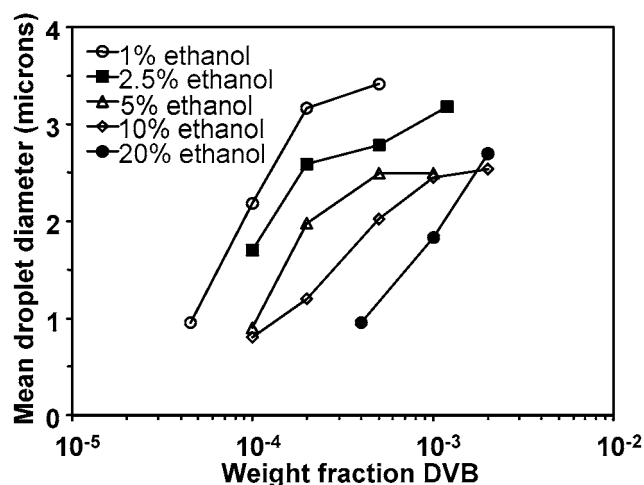

Figure 3. Mean DVB droplet diameter of the dispersions produced by the ouzo effect as a function of weight fraction DVB and weight percent ethanol in the final DVB–ethanol–water mixture.

miscibility limit or binodal curve; all solution compositions outside this line are a single phase. Note that a "reverse ouzo effect" region, producing small water droplets dispersed in DVB, exists on the opposite side of the two-phase region for DVB-rich systems, but this regime was tested only qualitatively.

It is helpful to consider the oil-to-solvent ratio in the following discussion, so dashed lines are used in Figure 2 to indicate ratios of 1:1000, 1:100, and 1:10. To the right of the stable ouzo region in Figure 2, the DVB is so concentrated that large droplets are formed upon addition of water; these droplets coalesce too rapidly to allow accurate droplet size measurements (using the Elzone analyzer). It is this spinodal decomposition region (or unstable ouzo region) where the CIPS process occurs. Note that the division between the stable ouzo region and the unstable ouzo region occurs at a DVB/ethanol ratio of approximately 1:20. The authors believe that the division between the stable and unstable ouzo regions occurs at approximately the same location as the spinodal curve. An attempt was made to calculate the spinodal curve using two thermodynamic models (NRTL and UNIQUAC). Unfortunately, lack of measured thermodynamic data on DVB, combined with the strong nonidealities of this three-component liquid system, made it impossible to calculate an accurate spinodal curve.

B. Mean Droplet Diameter. Droplet size distributions were measured for DVB–ethanol–water dispersions throughout the stable ouzo region (see Figure 2). This region corresponds to DVB/ethanol ratios from 1:20 to 1:1000 and final ethanol concentrations from 1 to 40 wt % after the addition of water. Figure 3 shows the mean droplet diameter of the dispersions formed by the ouzo effect as a function of weight fraction DVB for various ethanol concentrations. At fixed ethanol concentration, increasing the concentration of DVB causes the mean droplet diameter to increase. At DVB weight fractions larger than 2×10^{-3}, only large droplets which coalesce too rapidly to be measured are formed. In solutions with small oil-to-solvent ratios, so few oil molecules are near each nucleus that only very small droplets form. Conversely, with increasing oil-to-solvent ratios, more oil is near each nucleus, so larger droplets form.

When the two-phase dispersion is formed, some of the oil remains dissolved in the continuous water–ethanol phase and does not diffuse into the droplets. The con-
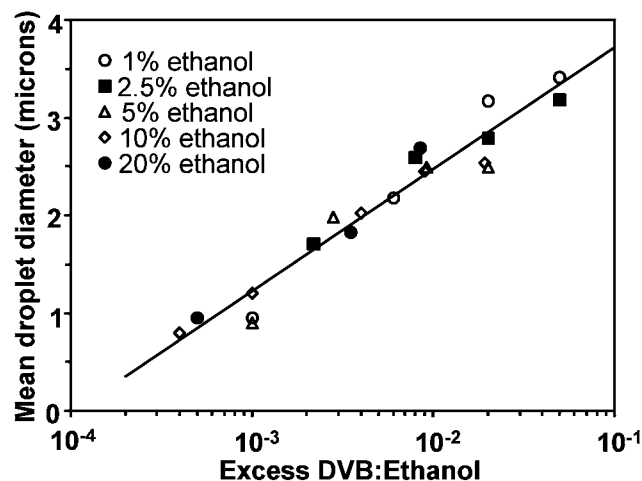
Figure 4. Same data in Figure 3 replotted to show that the mean DVB droplet diameter is primarily a function of one parameter: the excess DVB-to-ethanol ratio in the final DVB–ethanol–water mixture.
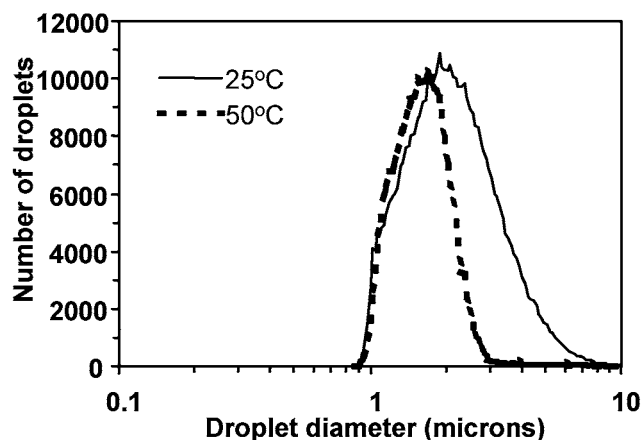

Figure 6. Number density of droplets formed by the ouzo effect as a function of DVB and ethanol concentrations, showing that adding additional water to decrease the weight fraction of ethanol causes the number density to decrease proportionately.

Figure 5. Histogram showing the droplet size distribution produced by the ouzo effect where the DVB/ethanol ratio = 1:200 and the concentration of ethanol after addition of water is 10 wt %: thin solid line, components are mixed and measured at room temperature, mean = 1.99 μm, standard deviation = 0.88 μm; heavy dashed line, components are mixed at 50 °C and then allowed to cool to room temperature before measurement, mean = 1.21 μm, standard deviation = 0.43 μm.

centration of the DVB which is soluble in the continuous phase increases with increasing ethanol concentration (see Figure 2). The concentration of oil in excess of its saturation concentration in the solvent + water continuous phase will be referred to as "excess oil". The data in Figure 3 are replotted in Figure 4 using the ratio of excess DVB concentration to ethanol concentration as the independent variable. One sees that the five curves in Figure 3 collapse to form a single line in Figure 4, indicating that the mean size of the droplets formed depends only on the ratio of excess oil concentration to solvent concentration in the system. The mean droplet diameter is *not* a function of the final ethanol weight fraction.

C. Droplet Size Distributions. Droplet size distributions produced by the ouzo effect in this study are log–normal, with standard deviations of approximately 40–80% of the mean. The width of the droplet size distribution is a function of temperature. Figure 5 shows two droplet size distributions for the DVB–ethanol–water system obtained at two different temperatures. The solid line distribution was produced when the components were mixed at room temperature, and the dashed line distribution was produced when the components were mixed at
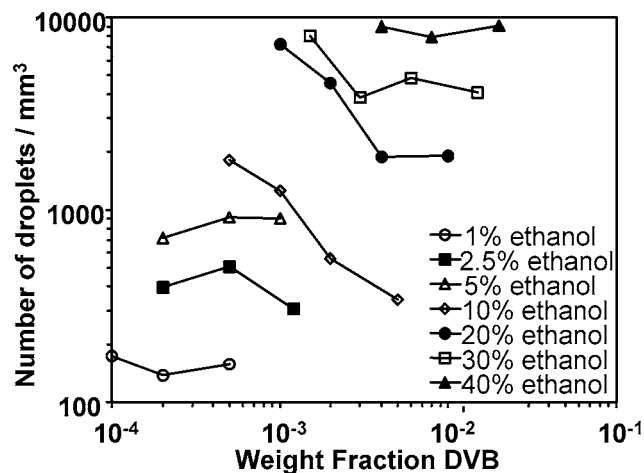
50 °C, followed by cooling in a water bath to room temperature. The 50 °C droplet size distribution clearly is narrower.

Since the solubility of the oil in the aqueous phase increases as temperature increases, there is less excess oil available to form droplets at elevated temperatures. Thus, on addition of water, smaller droplets are formed than would be formed from the same solution at room temperature. When the solution is cooled, more oil comes out of solution. However, cooling is a slow process compared to mixing and to diffusion, so the concentration of *excess* oil does not increase rapidly enough to cause supersaturation and nucleation of new droplets. Instead, the oil has sufficient time to diffuse to already existing droplets. Assuming Fickian diffusion of the new excess oil to the droplets, in a given time t, all droplets will absorb almost all of the new excess oil within a radius R, where R is given approximately by $R = (Dt)^{0.5}$, where D is the diffusion coefficient of the oil. Thus, each droplet will absorb approximately the same volume of oil, and the radius of the smaller droplets will increase more than the radius of the larger droplets. Therefore, the size distribution, which is measured by droplet diameter, becomes narrower. In addition, over longer time scales, the smallest droplets will disappear, their contents being absorbed into the larger droplets by Ostwald ripening.[16] This causes a further narrowing of the droplet diameter distribution.

The number density of the droplets in the dispersions was also measured. Figure 6 shows the number density of droplets (droplets/mm³) in the DVB–ethanol–water system as a function of DVB for various ethanol concentrations. The number density of droplets decreases as more water is added, that is, as the ethanol concentration in the final solution decreases. Thus, the addition of more and more water does not necessarily cause the nucleation of new droplets by increasing the supersaturation of the oil. Instead, after a certain point, the addition of more water simply causes dilution of the number density of the droplets as the volume of the solution increases but the number of droplets remains approximately the same. This implies that the droplet number density in the dispersion can be controlled somewhat independently of the mean droplet size.

D. Stability of the Dispersions. The stability of the dispersions formed by the ouzo effect is determined by

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both the size of the droplets formed and the density difference between the droplets and the continuous phase. If the density of the droplets is close to that of the continuous phase and if the droplets are small, bulk phase separation by creaming will be slow. In this study, the most stable dispersions formed by the ouzo effect were produced using oils whose densities are almost equal to that of the continuous phase and which are very insoluble in water. Oils which are very insoluble in water, such as DVB, will come out of solution to form droplets even at very low concentration of oil. The small concentration of oil in such systems slows growth of the droplets and also favors the production of small droplets. DVB was used as the oil in most of the quantitative studies of the ouzo effect presented here because it has low solubility in water, it has a density close to that of water, and it is readily polymerized to form solid microspheres.

The stability of the dispersions can also be affected by any nonhomogeneity in the system. If the droplets formed are not uniformly dispersed throughout the solution, the regions of high droplet concentration would coalesce rapidly into a bulk second phase. For dispersions formed by the ouzo effect, the droplets do appear to be uniformly distributed throughout the solution. This observation is consistent with the hypothesis that the droplets are formed by homogeneous nucleation. It is well-known that the rate of homogeneous nucleation is an extremely strong function of supersaturation. At small supersaturations, the rate of nucleation of droplets is unmeasurably small. In the ouzo effect, the supersaturation of the oil increases as water is added to the solvent solution. With increasing supersaturation, the nucleation rate increases exponentially. Nucleation ceases when diffusion of oil into the already nucleated droplets causes the supersaturation to decrease despite the addition of additional water.

Nucleation is a random process, so initially the droplets are not uniformly distributed. However, in those regions where droplets are few, diffusion of oil to these droplets is too slow to cause the supersaturation to decrease as the water is added, so nucleation continues. Thus, one obtains a dispersion of fairly uniformly spaced droplets. For the dispersions reported here, the average distance between the droplets is approximately 100 μm, that is, 20–200 droplet diameters.

E. Effect of Solvent. Different solvents for the oil can be used to create droplet dispersions by the ouzo effect. The solvent should be completely miscible with water (or whatever third component will be added to the binary solution to cause supersaturation); otherwise, it will separate into a second phase when water is added. This would allow the oil to simply partition into the continuous second phase without nucleating into droplets. For example, solvents such as 1-butanol and methyl ethyl ketone, even though they are very water soluble, did not produce an ouzo effect with DVB because they are not miscible with water in all proportions.

The effects of solvent properties on the droplet size distribution and the stability of the droplets were studied by comparing the results obtained using ethanol to those obtained using acetonitrile and dimethyl sulfoxide (DMSO) as solvents. Both water and DVB are completely miscible in all three solvents.

The mean droplet sizes of dispersions formed with 10% ethanol and 10% DMSO are shown in Figure 7. The droplet size obtained using DMSO as a solvent is very similar to that obtained using ethanol. Figure 8 shows that the droplet size obtained using acetonitrile is significantly larger than that obtained using ethanol. A close study of the droplet size distributions showed that the acetonitrile
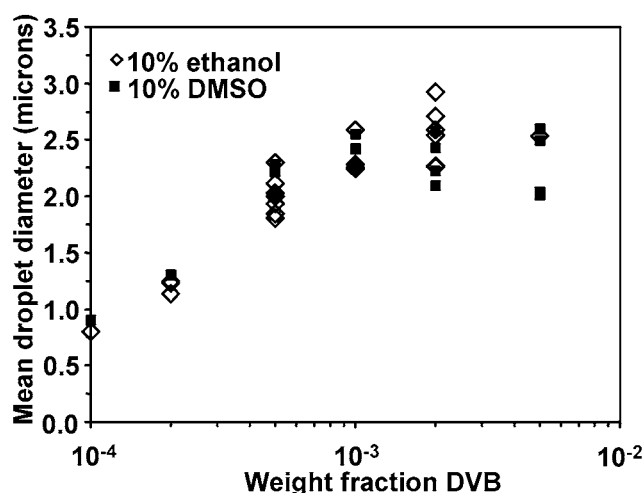

Figure 7. Mean DVB droplet diameter of the dispersions produced by the ouzo effect as a function of weight fraction DVB and in 10 wt % ethanol and DMSO mixtures. There is no significant difference in droplet size using either solvent.
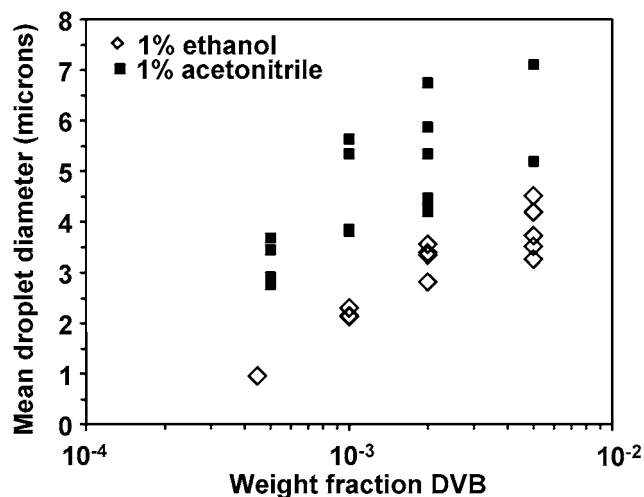

Figure 8. Mean DVB droplet diameter of the dispersions produced by the ouzo effect as a function of weight fraction DVB and in 1 wt % ethanol and acetonitrile mixtures. The DVB droplets produced using acetonitrile retain some of the solvent in the droplets and thus are larger.

Table 1. Density, Viscosity, and Diffusion Coefficient in Water for Three Solvents and DVB at 20 °C

	density (g/mL)	binary liquid diffusion coefficient in water[17,18] ($\times 10^{-5}$ cm²/s)	viscosity[19] (cP)
acetonitrile	0.785	1.26	0.35
DMSO	1.095	0.64	1.10
ethanol	0.787	1.00	1.22
DVB	0.914		

size distributions are significantly wider, on the large droplet side.

The binary liquid diffusion coefficients and viscosities of the three solvents are given in Table 1. Since acetonitrile has the highest diffusion coefficient and lowest viscosity, one would expect the mixing of acetonitrile in water to be the fastest. Fast mixing should lead to more uniform

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supersaturation and smaller droplets; thus, mixing rate is not the cause of the larger droplets produced using acetonitrile. Instead, it is likely that the larger droplets are due to acetonitrile remaining in the dispersed phase. To obtain a rough measure of the relative affinity of the three solvents for the water versus the oil phase (DVB), the partition coefficients in the three solvents were measured. Mixtures of 45 wt % water, 45 wt % DVB, and 10 wt % solvent were mixed well and then allowed to separate for 48 h in a buret. The partition coefficients were then determined from the masses of the aqueous and organic phases formed, assuming that negligible amounts of water were dissolved in the DVB-rich phase and vice-versa. The partition coefficients, defined as the ratio of the weight fraction of solvent in the aqueous phase to that in the organic phase, were 6.9, 6.8, and 1.0 for ethanol, DMSO, and acetonitrile, respectively. Thus, acetonitrile will partition approximately evenly between the aqueous and dispersed phases, whereas ethanol and DMSO will partition nearly exclusively into the aqueous phase, leaving pure DVB droplets. Since the droplets formed with acetonitrile will likely contain some of the solvent as well as the DVB, these droplets are larger than the almost pure DVB droplets formed with the other two solvents.

Droplet dispersions remain stable (i.e., do not cream rapidly) when the droplet size is small and/or the densities of the dispersed and aqueous phase are similar. When acetonitrile partitions into DVB droplets, the density of the dispersed phase is reduced, thus lowering the dispersion's stability. Further, the droplets formed with acetonitrile are larger than those formed with the other two solvents, also causing the dispersions to cream more rapidly. Qualitatively, bulk phase separation occurred approximately twice as fast in the acetonitrile systems when compared to the ethanol or DMSO systems. By changing the oil to one whose density is very near that of water, fluorostyrene (0.98 g/mL), we were able to make dispersions formed by the ouzo effect which were stable for several days!

5. Conclusions

The ouzo effect is a technique useful for forming dispersions of liquid droplets in a continuous liquid phase, without the use of surfactants, dispersing agents, or mechanical agitation. A wide variety of oils and solvents can be used to tailor the droplets for use in a particular application. Oil-in-water and water-in-oil dispersions can be produced. In both cases, the ouzo effect will produce stable droplet dispersions if the oil is very insoluble in water. For an oil-in-water dispersion, a suitable solvent would be one which dissolves the oil but is also miscible with water in all proportions. The droplet size will be smaller when one uses a solvent which (after the addition of water) partitions primarily into the aqueous phase.

The mean droplet diameter of the dispersions produced by the ouzo effect is a linear function of one primary parameter, the excess oil-to-solvent ratio. The number density of the droplets can be varied independently from the mean droplet size by varying the amount of water added. The width of the size distribution can be narrowed by mixing the components at a higher temperature and then allowing them to cool to room temperature.