

Surfactant-Free Microemulsions in Fragrance Tinctures

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Accepted for publication February 11, 2021.

Synopsis

Tinctures are alcoholic or hydroalcoholic solutions prepared from vegetable or chemical substances. The concentration of the solute varies up to a maximum of 50%, e.g., vanilla tincture. Tinctures are very useful in the perfume industry because they contain ethanol, which can dissolve molecules such as fragrant molecules, and consequently form hydroalcoholic formulations together. Recently, we have shown that nanostructures exist in the monophasic water–ethanol–citronellol system, and it is therefore a question whether such nanostructures exist in a system where a perfume molecule of citral is present as the oil component instead of citronellol. In this study, the single-phase region was mapped conductometrically and then measured by Dynamic Light Scattering (DLS) and UV/Vis spectroscopy to determine the presence of nanostructures similar to classical microemulsions.

In early 1970s, Barden's group began working on microemulsions without the presence of a surfactant. They were the first to characterize such solutions with many methods and experiments (1). Later, microemulsions without the presence of a surfactant become a significant medium for various enzyme-catalyzed reactions as well as other chemical reactions. For example, Zoumpanioti et al. (2) studied the catalytic activity of lipases trapped in ternary systems without surfactants, consisting of water, short-chain alcohol, and hexane. Both enzymes effectively catalyze the esterification of acids. The authors have shown that the stability of encapsulated enzymes at low water contents in the system is higher than that found in microemulsions with classical surfactants.

We have recently shown that nanostructures exist in microemulsions without surfactants based on fragrance tinctures, composed of monophasic water–ethanol–citronellol mixtures (3). Consequently, the question of the existence of such nanostructures in other perfume tinctures arises. To answer that question, we have formulated tinctures with citral molecules that are structurally very similar to citronellol molecules.

In recent years, static and dynamic percolation models for describing the microstructure of microemulsions have become very common. In the static percolation theory, the result

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of percolation is considered to be the formation of a bicontinuous phase, whereas in the dynamic percolation model, micelles are formed and ions are exchanged as a result of a "fusion" reaction (4–6).

Both models consider that percolation occurs when the critical amount of the aqueous phase in the single-phase system ϕ_w^p is reached, the so-called percolation threshold. The connecting law between the electrical conductivity and the concentration of the aqueous phase in a single-phase system before and after the percolation threshold ϕ_w^p with its critical coefficients is shown in the literature (7).

In this article, a nanostructural transition based on the percolation theory of a surfactant-free microemulsion composed of citral, ethanol, and water has been studied by measuring electrical conductivity, DLS, and UV/Vis spectroscopy.

EXPERIMENTAL

Ethanol (Aldrich, p.a.) and citral (Aldrich, p.a.) without prior purification and redistilled water were used to prepare the mixed solvent. Mixed solvents of different mass compositions were prepared in glass vials by adding the individual components by weighing. The monophasic region in the ternary phase diagram was determined by adding a specific mass of water with a syringe to the initial mass of the mixed solvent of ethanol and citral until the phase separation occurred, thus constructing a binodal curve. Measurements were performed in a thermostatic bath at 298.15 K.

A Wayne Kerr device, type 6430 A (Wayne Kerr, London, United Kingdom), was used to measure the resistance of working solutions. Its measurement accuracy is 0.02%, the voltage can vary in the range from 0 to 2 V, and the frequency can vary from 20 Hz to 500 kHz. The Anton Paar Litesizer 500 (Anton Paar, Graz, Austria) was used to measure the hydrodynamic radii. Before each measurement, the microemulsion solutions were filtered through a 0.2- μm filter. Agilent Cary 60 two-beam spectrophotometer (Agilent Cary, Santa Clara, CA) and a 1.0-cm-wide cuvette were used for measurements.

RESULTS AND DISCUSSION

Figure 1A shows the results of determining the separation region of the two-phase and single-phase regions, and the binodal curve of the ternary citral–ethanol–water system at 298.15 K. The experimental data are in agreement with those in the literature (8).

The plot of κ versus ϕ_w at $R_{E/C} = 2.3$ shown in Figure 1C represents a typical example of percolation phenomena. The conductivity is initially low, indicating the existence of discrete inverse micelles in a single-phase system. As the proportion of water in the inverse micelle system increases and when the percolation threshold is reached, there is a sharp increase in electrical conductivity. A sharp increase in electrical conductivity above the percolation threshold and linear growth with a further increase in the water content in the system result in two possible effects: either the formation of microemulsion aggregates and charge changes by the fusion reaction between them or the existence of the bicontinuous phase which forms free channels for charge exchange. From the calculation of the experimental data, the obtained result for the critical percolation coefficient ν is 0.80 for the experimental path $R_{E/C} = 2.3$ (Figure 1D), indicating the presence of a

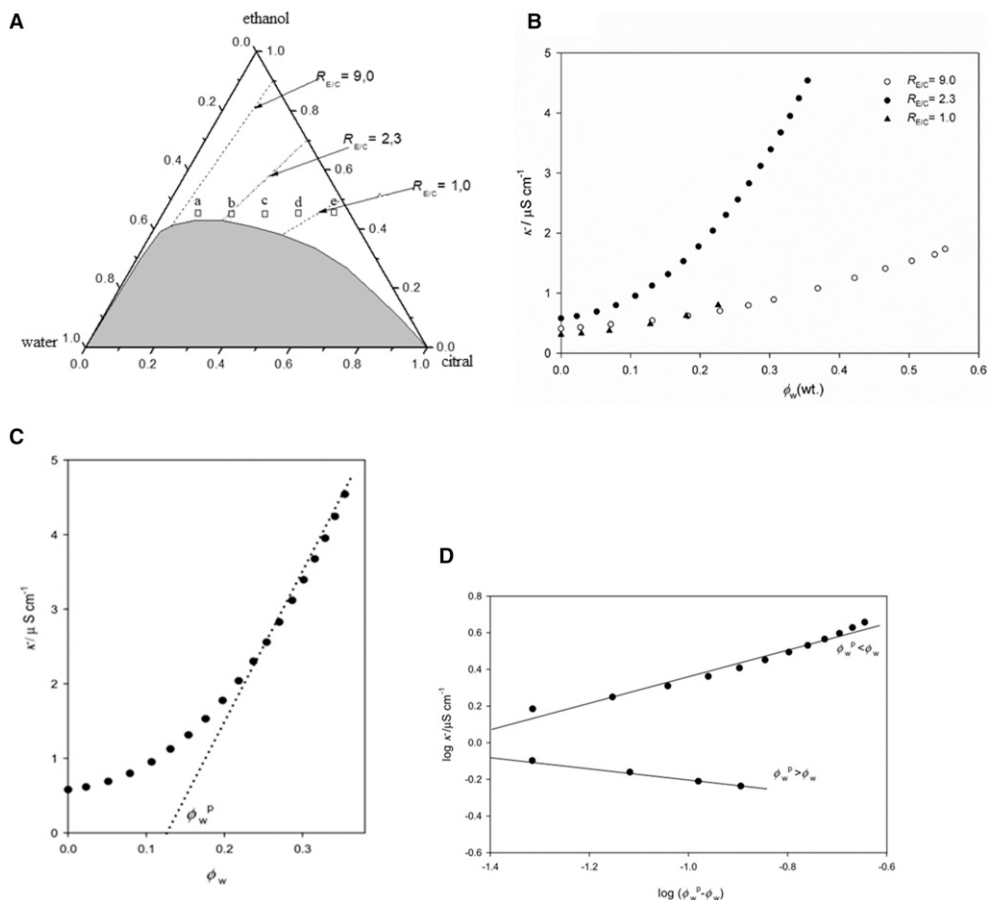


Figure 1. (A) Ternary phase diagram of citral–ethanol–water at 298.15 K, where the white area represents a single-phase, macroscopically homogeneous system, whereas the gray area represents a two-phase system. The squares refer to selected samples (A–E) of the single-phase ternary citral–ethanol–water system at 298.15 K for measuring DLS. (B) The conductometric mapping of a single-phase ternary citral–ethanol–water system at 298.15 K refers to the experimental paths shown by the dashed lines in (A). (C) The dependence of electrical conductivity on the mass fraction of added water in a single-phase ternary citral–ethanol–water system at 298.15 K at a constant ratio of the mass fraction of ethanol and citral, $R_{E/C} = 2.3$. (D) The variation of $\log \kappa$ versus weight fraction of water along the dilution line $R_{E/C} = 2.3$ above and below the percolation threshold.

dynamic percolation model. That is, a micelle barrier layer or possible microemulsion aggregates are formed by short-chain alcohol as a surfactant, although a certain amount of water molecules may permeate it due to the interaction of hydrogen bonds between water and ethanol (3). Based on the experimental data, the calculated value for the coefficient p above the percolation threshold is 0.32 (Figure 1D), and as such cannot be attributed to either static or dynamic percolation model because the obtained value for the coefficient p is not in accordance with the theoretical value. The main reason for this is that at values above the percolation threshold ϕ_w^p , due to the intramolecular interaction caused by hydrogen bonds, more and more water molecules penetrate the barrier layer of short chain alcohol with increasing mass fraction of water (3,9). Similar to that in the citronellol system, the short-chain alcohols are not able to form an effective barrier layer of microemulsion-like structure. They can only form a solution containing hydrogen-bonded

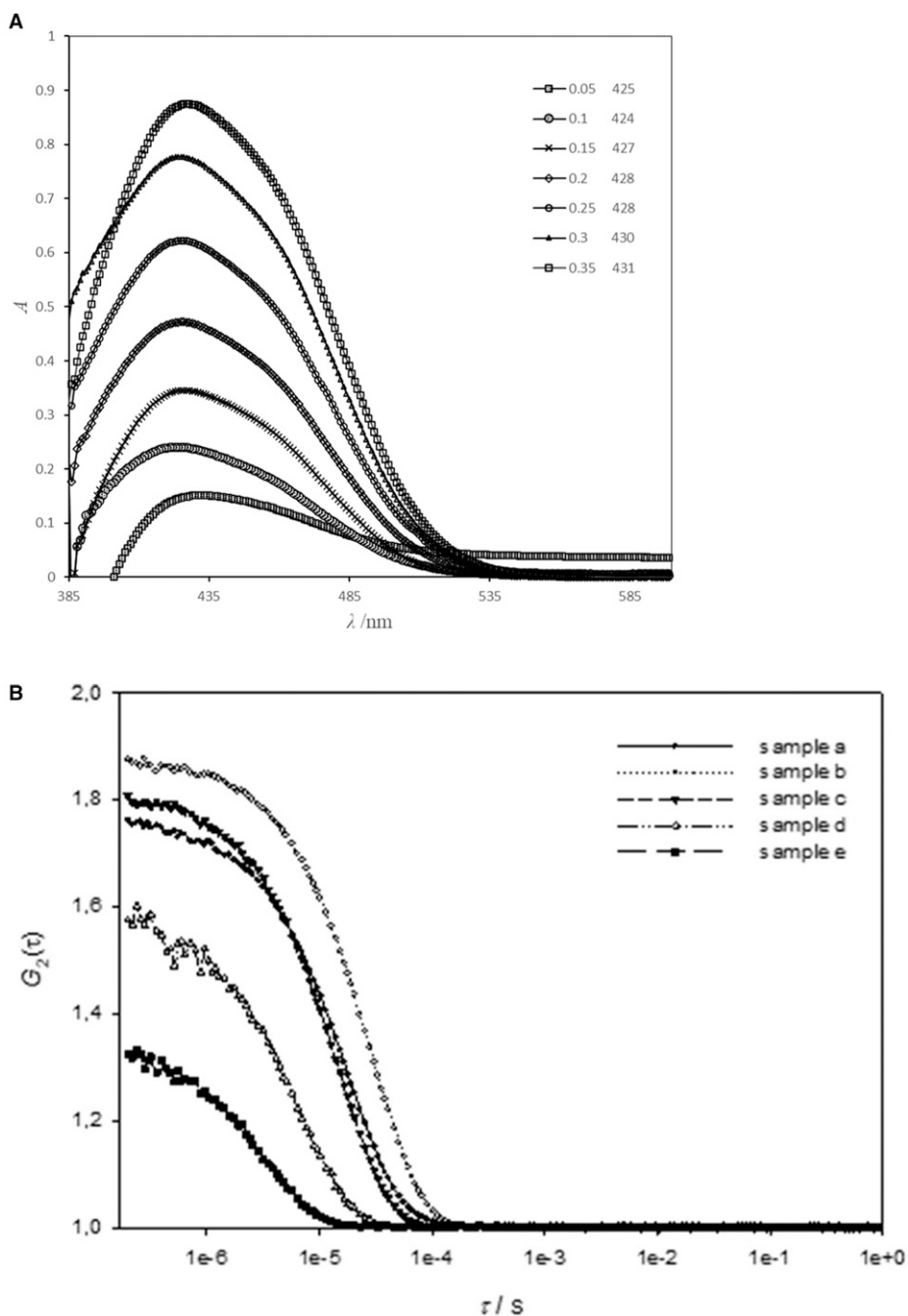


Figure 2. (A) Absorption of aqueous solutions of methyl orange in a ternary mixture of citral–ethanol–water at a constant ratio of mass fractions of ethanol and citral ($R_{E/C} = 2.3$) and different proportions of added aqueous solutions of methyl orange (ϕ_w), where the concentration of the methyl orange solution is $c = 0.1 \text{ mmol L}^{-1}$. (B) Time-dependent self-correlation functions as obtained by DLS for prepared samples (Figure 1A). The size of particles is calculated from well-defined correlation functions only.

aggregates of water molecules and short-chain alcohols, where molecules of citral are present inside or on edges (3).

The microstructure of the environment within the microemulsion aggregates can be determined by UV-Vis spectrophotometric measurements using a solvatochromatic probe. By increasing the proportion of aqueous solution of methyl orange in the microemulsion (Figure 2A), the absorption maximum of methyl orange was shifted to the side of higher wavelengths, indicating a higher polarity of the medium. As expected, the absorption maximum of methyl orange increases in the range of 425–431 nm (Figure 2A). The absorption maximum of methyl orange is 465 nm in pure water and 407 nm in ethanol. These results show that the polarity of the dissolved methyl orange environment is between water and ethanol values, and the results are in agreement with those in the literature (3,10–13).

Figure 2B) shows that the correlation becomes increasingly more pronounced the closer the path is to the best percolation path ($R_{E/C} = 2.3$) obtained from conductometric measurement. Then, the calculated hydrodynamic radii from DLS measurements assuming a spherical geometry show the increase in size (for, e.g., sample b hydrodynamic radii are around 9 nm) near the cross section with the best percolation conductivity path. The results agree with the results found in the literature (3,11,14).

CONCLUSIONS

Classical microemulsion systems often used the dynamic percolation model. In that case, main explanation is that systems have a weak interfacial film at low water content and below the threshold of appearance of a second regime of conductivity, but this model and the static one cannot fit the conductivity data of the second regime. The main reason for this is that at values above the percolation threshold, due to the intramolecular interaction caused by hydrogen bonds, more and more water molecules penetrate the barrier layer of short-chain alcohol with increasing mass fraction of water.

Furthermore, DLS experiments show that the correlation becomes increasingly more pronounced the closer the path is to the best percolation path ($R_{E/C} = 2.3$). Then, the calculated hydrodynamic radii from DLS measurements assuming a spherical geometry show the increase in size near the cross section with the best percolation conductivity path. The presence of nanostructure may affect the chemical and biological stabilities of fragrance molecules in such hydroalcoholic solutions and could be used as nanodomains for stabilization of fragrance molecules, which can reflect on the vapor pressures of the different components.

ACKNOWLEDGEMENT

This work was funded by Croatian Science Foundation, project number UIP-2017-05-6282.

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