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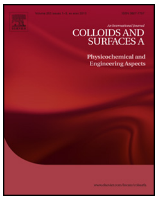

Evaporation triggered self-assembly in aqueous fragrance–ethanol mixtures and its impact on fragrance performance

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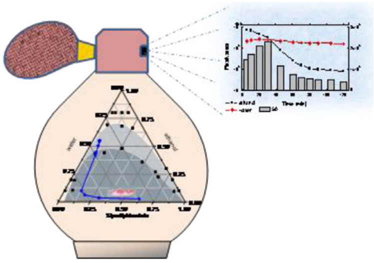
HIGHLIGHTS

- Evaporation path of ternary water–ethanol–fragrance systems is located in phase diagram.
- When surfactant-free microemulsions form, the fragrance activity is enhanced.
- Drying in the two-phase region triggers spontaneous retention of fragrance.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study demonstrates how the evaporation of a ternary ethanol–water–fragrance solution leads to a transition from an unstructured ternary ethanol-rich solution, to a structured water-rich solution by crossing the so-called pre-ouzo region of its phase diagram. The exothermal nature of this self-assembly revealed by calorimetry suggests that it is coupled to molecular transfer between coexisting micro-domains.

Surprisingly, fragrance evaporation is first accelerated in the pre-ouzo region as evidenced unambiguously by simultaneous on-line gravimetric, calorimetric and gas chromatographic monitoring during drying. Upon further drying, a transition from the pre-ouzo to the two-phase turbid region of the phase diagram is observed as the loss of water becomes more important that of ethanol. At this stage, the size of the fragrance-rich domain increases by three orders of magnitude as fragrance droplets surrounded by ethanol molecules are entrapped in water-rich external media and the fragrance evaporation is depressed.

This initial acceleration and subsequent retardation of the evaporation kinetics of fragrance molecules are general for all perfumery ingredients. The path of the compositional change in the phase diagram during evaporation is investigated under strong inert gas flux for the first time to our knowledge by two combining on-line methods.

1. Introduction

An ethanol-containing fragrance solution can be considered as a ternary mixture of volatile molecules, namely ethanol, water and fragrance ingredients. The evaporation kinetics of such a system depends on the composition of the ethanol–water mixture and on the solubility of fragrance ingredients in it. During its evaporation, the composition of the liquid solution changes spontaneously, leading to variable concentration ratios between the three components. This results in a well-defined "path" followed by evaporation on the ternary phase diagram of the system. The compositional change of the solution influences the thermodynamic activity coefficient and therefore the partial vapor pressure of its ingredients, affecting eventually the olfactory performance of the perfume. It is already known since a long time that evaporation of the most volatile

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component does not always occur first. This phenomenon has already been observed and has been described in detail by Rechenberg in his textbook [1]. Later, this effect has been known under the name of “solutropy”, described in detail by Vriens and Medcalf [2] but to our knowledge never explained by a predictive model taking into account microstructures. What is certain is that the order of evaporation of solutes from alcoholic solutions does not follow volatility and therefore cannot be predicted taking into account intrinsic properties of components ($\log p$, pure solvent evaporation enthalpy, Hildebrandt parameters or similar). The same effect was subsequently investigated by Ostwald when establishing the equation of state of ternary solutions in his Nobel Prize work. Although ethanol–water–fragrance systems can be considered as simple ternary mixture, a physical investigation of their evaporation and its consequence on fragrance performance is scarce.

On the other side, water–ethanol systems are known to form azeotropic mixture with properties associated to non-ideal mixing. This behavior for example is expressed by the unusual shape of the enthalpy of mixing which exhibits a minimum at a given ethanol mole fraction, as observed by Lama and Benjamin in 1965 [3] and confirmed later by Boyne and Williamson [4], and Franks [5].

Dixit et al. [6] demonstrated using neutron diffraction the presence of structures at the molecular scale in concentrated binary ethanol–water solutions with a molar ratio of 7:3. They proved that mixing at molecular level is incomplete because water molecules are well arranged around the closed-packed methyl group of clustered ethanol molecules. Dougan et al. [7] observed a similar behavior in the methanol–water systems. Molecular dynamics study [8] of vaporization enthalpies, static dielectric constants and self-diffusion coefficients of these liquids highlighted the existence of a minimum of the ethanol mobility at low molar concentrations of ethanol and of water clustering at high ethanol concentrations. An inflection point was found on the surface tension curve of ethanol–water solutions at ethanol molar fraction of 0.1. Before this critical point, the water-rich solution is bad solvent for the ethanol because of the strong hydrogen bond network of the water molecules. The ethanol molecules adsorbed at the interface decreasing the surface tension of water and the surface excess of the ethanol molecules increases. Beyond the critical molar fraction of ethanol, the surface excess decreases in the sense of Gibbs, showing weakening of the molecular interactions in the solution. The bulk solution progressively transforms to a good solvent for the ethanol above this point [9]. It has been shown that the critical point corresponds to the transition from finite ethanol clusters to an infinite three dimensional network of hydrogen bonded ethanol molecules, as summarized by Zana [10].

Further investigations of ternary systems composed of water, alcohol and nonpolar additive have revealed the formation of aggregates with different size in the different domains of the phase diagram [11,12]. Studies of ternary mixtures based on toluene, water and 2-propanol [13] have highlighted the existence of aggregates similar to swollen micelles in the pre-ouzo region, which is separated by a well-defined binodal line from the two-phase ouzo-region [14]. Whether pre-ouzo region is or is not enclosed between a binodal and a spinodal line is still under discussion [15]. Direct light [16], X-ray and neutron scattering characterization on absolute scale was since used to confirm the formation of transient 2 nm sized aggregates that follow all characteristics of microemulsions according to IUPAC definition, but contain no surfactant. It is expected that those surfactant-free microemulsion domains have shorter life-time than surfactant based-microemulsions of the same size [13], but this has not yet experimentally proven to our knowledge. The same effect has been confirmed with other ternary mixtures in which components 1 and 2 are mutually miscible and component 3 is only miscible in one of them. Non-miscibility of two of the components associated to variable distribution coefficient of ethanol is the key point in the behavior described in this paper. This holds in an ethanolic fragrance solution as well, where ethanol and water are mutually miscible but fragrance ingredients are only soluble in ethanol.

Following the recent demonstration of the existence of nanostructures in water/ethanol/1-octanol systems, Kunz and coworkers have extended the investigation to perfume tinctures. In this case also, the existence of nano-droplets with a radius of 2–3 nm was demonstrated using dynamic and static light scattering to locate the de-mixing boundary between the transparent and turbid domains of the phase diagram [17]. In the biphasic region, the emulsion droplets are three orders of magnitude larger in radius since in the ouzo region droplets are typically a few micrometers radius while in the pre-ouzo region, equilibrium size is only 2–3 nm. This corresponds to three orders of magnitude in radius, i.e. nine orders of magnitude larger in number of molecules per perfume rich domain. A domain of a few hundred fragrance molecule per aggregate in the pre-ouzo region grows thus over 10^{11} molecules per domain in the ouzo region.

In the present study, this concept is further developed to investigate the impact of these nanostructures on the fragrance performance during the evaporation of ternary systems based on three volatile compounds, namely water, ethanol and one or several fragrance ingredients. For this purpose, we intend to correlate the initial ternary composition to the formation of nanostructures and to the fragrance performance during the evaporation process. Important fragrance performance effect is the so-called “blooming” which corresponds to an increase in vapor pressure, as opposed to the effect observed when entrapping a fragrance to extend its lastingness. The former translates into an increase of the activity coefficient of fragrance ingredients and the latter typically to a decrease of the same coefficient. We believe that this study is able to provide guiding principles for the formulation of successful alcoholic fragranced products such as eau de toilette, eau de perfume, aftershaves, eau de cologne, body mists.

2. Materials and methods

2.1. Simultaneous thermogravimetry (TGA), differential scanning calorimetry (DSC) and gas chromatography (GC–MS) analysis

The evaporation kinetics and vapor–liquid compositions were monitored with a single instrument combining four different analytical methods, namely thermogravimetry (TGA), differential scanning calorimetry (DSC), gas chromatography (GC) and mass spectroscopy (MS). The simultaneous analysis of different parameters provides information about the physical state of the investigated solutions and their gas phase as function of time and temperature and under controlled gas flows. A schematic presentation of TGA–DSC_GC–MS instrument is provided in Fig. 1.

The Labsys-Evo Robot (Fig. 1A) is a product of Setaram Instrumentation (Caluire, France) which works either in TGA mode only or simultaneously in TGA and DSC mode. By measuring in TGA–DSC mode it is possible to link the thermogravimetric analysis to the heat flow and temperature measurement. The isothermal temperature accuracy is ±1 °C, weighting precision is ±0.01%, and furnace heating typically 20 °C per minute between ambient and water/ethanol boiling temperature.

First, the studied sample is inserted in an aluminum crucible and its initial weight is measured with a laboratory balance. Then, the measured sample and an empty crucible (reference) are automatically placed on the TGA balance plate by the robot hand. The furnace is automatically closed and heated to the desired temperature. Once the temperature is stabilized, the TGA–DSC measurements are started following the experimental procedure, determined in advance by the user.

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