# Is spontaneous emulsification in ternary solutions a common occurrence in nearly miscible solvents, or is it an urban legend caused by unavoidable impurities?

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We consider pairs of solvents that are not fully miscible with each other, such as water and octanol, water and ethyl acetate, fatty phosphoric acids and water, and water and 2-butanol. All of these have miscibility gaps that can be 'closed' at room temperature by adding a third compound. Depending on the context and the amount required to close the miscibility gap, this third component can be a co-solvent, a hydrotrope or an antagonistic salt.
The recently developed 'Gouy' method, which uses Static Light Scattering (SLS) in absolute units (the Rayleigh ratio expressed in $cm^{-1}$), enables the determination of both the apparent radii and the number concentration of droplets formed by slow dilution within the single-phase domain. This effect has been observed many times and is sometimes attributed to critical fluctuations only. The rest of the reported observations were dismissed as urban legends or attributed to the presence of impurities.
However, ultra-sensitive light scattering (micro-Rayleigh, software-filtered) reveals that critical fluctuations are consistently present near the critical point. In most cases investigated using the Gouy method with static light scattering, two types of aggregates are always found far from the critical point when the solvent is a solvo-surfactant or the surface-active species is an electrolyte.
The smaller aggregates, with a diameter of a few nanometres at most, have been named 'pre-ouzo' solvent-free microemulsion (SFME) aggregates. These aggregates are due to the competition between entropy and hydration forces[1].
A smaller number density of larger spontaneous aggregates, always between 50 and 400 nm in diameter, is also often reported. We argue that spontaneous emulsification results from favourable combinations of three factors: (i) the configuration entropy of large droplets, (ii) surface tension effects related to surface-active electrolytes, and (iii) the entropy cost of microphase separation. The aforementioned three mechanisms involved in the formation of large droplets in ternary fluids, reported as monophasic systems, have been quantified by H. Reiss[2], A. Onuki[3] and S. Marcelja[4]. We propose that these large, spontaneous emulsion droplets are present in ternary systems for thermodynamic reasons, meaning they are not merely an urban legend or an effect due to uncontrolled impurities.

**Keywords:**
Nano-ions ; antagonistic salts ; hydrotropes ; critical phenomena ; entropy ; emulsification

**References:**

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