



Mesoscale solubilization and critical phenomena in binary and quasi-binary solutions of hydrotropes



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ABSTRACT

Hydrotropes are substances consisting of amphiphilic molecules that are too small to self-assemble in equilibrium structures in aqueous solutions, but can form dynamic molecular clusters H-bonded with water molecules. Some hydrotropes, such as low-molecular-weight alcohols and amines, can solubilize hydrophobic compounds in aqueous solutions at a mesoscopic scale (~ 100 nm) with formation of long-lived mesoscale droplets. In this work, we report on the studies of near-critical and phase behavior of binary (2,6-lutidine–H₂O) and quasibinary (2,6-lutidine–H₂O/D₂O and tert-butanol/2-butanol–H₂O) solutions in the presence of a solubilized hydrophobic impurity (cyclohexane). In addition to visual observation of fluid–phase equilibria, two experimental techniques were used: light scattering and small-angle neutron scattering. It was found that the increase of the tert-butanol/2-butanol ratio affects the liquid–liquid equilibria in the quasi-binary system at ambient pressure in the same way as the increase of pressure modifies the phase behavior of binary 2-butanol–H₂O solutions. The correlation length of critical fluctuations near the liquid–liquid separation and the size of mesoscale droplets of solubilized cyclohexane were obtained by dynamic light scattering and by small-angle neutron scattering. It is shown that the effect of the presence of small amounts of cyclohexane on the near-critical phase behavior is twofold: (1) the transition temperature changes toward increasing the two-phase domain; (2) long-lived mesoscopic inhomogeneities emerge in the macroscopically homogeneous domain. These inhomogeneities remain unchanged upon approach to the critical point of macroscopic phase separation and do not alter the universal nature of criticality. However, a larger amount of cyclohexane generates additional liquid–liquid phase separation at lower temperatures.

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1. Introduction

Hydrotropes are substances consisting of amphiphilic molecules whose non-polar part is much smaller when compared with long hydrophobic chains of traditional surfactants [1,2]. Typical examples of non-ionic hydrotropes include short-chain alcohols and amines. In aqueous environment, hydrotropes unlike surfactants do not spontaneously self-assemble to form stable equilibrium micelles [3], although they are frequently used as “co-surfactants” to stabilize micro-emulsions [4]. However, above a

certain concentration, hydrotrope solutions may exhibit dynamic, non-covalent molecular clustering that may be viewed as “micelle-like” or structural fluctuations [5–13]. Molecular dynamics studies show that the clusters of hydrotrope molecules, hydrogen-bonded with the aqueous surrounding, are short-ranged (order of 1 nm in size) and short-lived with a lifetime of tens or hundreds picoseconds [10–12]. This molecular clustering, usually involving hydrogen bonds with water molecules, can cause distinct thermodynamic anomalies, such as those observed in aqueous alcohol solutions in water-rich region [11,14–19].

In addition, many experiments on aqueous solutions of hydrotropes show the presence of long-lived mesoscale inhomogeneities of the order of a 100 nm in radius [12,13,20–32]. It has been shown that such inhomogeneities occur in aqueous solutions of nonionic hydrotropes when the solution contains a third, more

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hydrophobic, component [12,13,28–32]. Remarkably, these inhomogeneities (emerging in water-rich ternary systems) are only pronounced in the hydrotrope concentration range where molecular clustering and thermodynamic anomalies are observed in the original binary hydrotrope–water solutions. The hypothesized structure of these mesoscopic droplets is such that they have a hydrophobe-rich core, surrounded by a H-bonded shell of water and hydrotrope molecules [12,13,22,31,32]. These droplets can be extremely long-lived, being occasionally stable for over a year [32]. The phenomenon of the formation of mesoscopic inhomogeneities in aqueous solutions of nonionic hydrotropes induced by hydrophobic “impurities” is referred to as “mesoscale solubilization” [12,13,31,32]. Mesoscale solubilization may represent a ubiquitous feature of certain nonionic hydrotropes that exhibit molecular clustering in water and may have important practical applications in areas, such as drug delivery, if the replacement of traditional surfactants is necessary.

Mesoscale solubilization is still poorly understood and a theory for this phenomenon is yet to be developed. If such a system is brought into the vicinity of the liquid–liquid critical point, mesoscale solubilization could somehow interact with the mesoscopic concentration fluctuations [31]. The first studies of the mesoscale solubilization near the liquid–liquid separation in ternary solutions of *tert*-butanol, propylene oxide and water were performed by Sedláč and Rak [30] and by Subramanian et al. [31]. These works agree on the interpretation of the observed mesoscale inhomogeneities as the phenomenon of solubilization of oily impurities originally present in *tert*-butanol and propylene oxide. However, behavior of these inhomogeneities in the critical region remained unclear. Subramanian et al. [31] speculated that the mesoscale droplets could exhibit anomalous curvature fluctuations in the critical region, thus forming a sponge phase. Herzog et al. [33] have demonstrated that a bicontinuous interface can be stabilized with the help of colloidal particles, which are wetted in both phases. It was thus hypothesized that the mesoscopic droplets, which might behave as colloidal particles, could stabilize the bicontinuous phase formed in hydrotrope–water–oil systems near the critical point. This is one possible scenario. An alternative possibility is the aggregation or disintegration of solubilized droplets caused by attractive Casimir forces induced by the concentration fluctuations [34].

There are two main obstacles preventing quantitative studies of mesoscale solubilization near phase separation and, in particular, in the critical region. Firstly, mesoscale solubilization could be easily confused with the so-called “ouzo effect” [35,36], the formation of micron-size metastable droplets (making the solution milky-white) by nucleation between the thermodynamic solubility limit (binodal) and the absolute stability limit of the homogeneous phase (spinodal). Moreover, mesoscale solubilization and the ouzo effect may overlap, thus making unambiguous interpretations of the experiments challenging. Secondly, in the critical region this task will require simultaneous measurements of

two mesoscopic lengths, the correlation length of the critical fluctuations and the size of the mesoscopic droplets. This task cannot be accomplished by light scattering experiments alone. When the correlation length reaches 20–30 nm, the critical opalescence dominates the light-scattering intensity and the size of the mesoscale droplets becomes poorly detectable. Refractive-index matching is not applicable for this particular case because of the large difference between the refractive indices of oil and water. The problem can be solved in small-angle neutron scattering (SANS) experiments by changing the H₂O/D₂O ratio, such that the signal from the SANS scattering caused by the critical fluctuations can be almost eliminated.

In this work we report the results of dynamic light scattering (DLS) and SANS experiments on binary solutions, 2,6-lutidine–H₂O, and ternary (quasi-binary) solutions, 2,6-lutidine–H₂O/D₂O and *tert*-butanol/2-butanol–H₂O. All these systems contain hydrotropes: 2,6-lutidine, *tert*-butanol (TBA), and 2-butanol (2BA), and all exhibit critical phase separation. Critical phenomena in aqueous solutions of 2,6-lutidine were studied earlier in detail [37–42]. Liquid phase separation in this system was also studied in the presence of colloid particles [34,43]. In particular, attractive Casimir forces between colloid particles, induced by the concentration fluctuations, were discovered for this system [34].

The systems 2,6-lutidine–H₂O/D₂O and TBA/2BA–H₂O can be considered as a “quasi-binary”. Mixtures of isotopes, H₂O/D₂O, as well as of isomers, TBA/2BA, form near-ideal solution and can be regarded as effective compounds whose properties can be tuned by changing the component ratio. In particular, the two butanol isomers are very similar, except for the fact that 2BA exhibits partial immiscibility with water, while TBA is the highest molecular-weight alcohol to be completely miscible with water under ambient conditions. TBA is a “perfect” hydrotrope. When placed at the water/oil interface, a TBA molecule is equally divided, with the hydroxyl group on the water side and the methyl groups on the oil side [44]. It was expected that on addition of TBA to 2BA the immiscibility gap in the TBA/2BA–H₂O system would shrink and a liquid–liquid critical point could emerge. We have confirmed this expectation. Moreover, we have shown that an increase of the TBA/2BA ratio affects the liquid–liquid equilibria in the quasi-binary system at ambient pressure in the same way as the increase of pressure modifies the phase behavior in binary aqueous solutions of 2BA [45–47].

We were able to simultaneously measure the correlation length of the critical fluctuations near the liquid–liquid separation and the size of the mesoscopic inhomogeneities. It is shown that the effect of the presence of small amounts of a hydrophobe (controlled addition of cyclohexane) on the near-critical phase behavior is twofold: (1) increase of the domain of liquid–liquid separation; (2) formation of long-lived mesoscopic inhomogeneities that survive and remain basically unchanged near the critical point of macroscopic phase separation. The presence of these inhomogeneities does not alter the universal nature of critical anomalies.

Table 1
Chemicals.

Chemical Name	Source	Purity (mass fraction)
TBA (2-methylpropan-2-ol) (UMD)	Alfa Aesar	0.998
2BA (butan-2-ol) (UMD)	Sigma–Aldrich	0.995+
Cyclohexane (CHX) (Moscow)	Merck	0.98
Cyclohexane (CHX) (UMD and NIST)	Baker	0.999
Milli-Q water (UMD and NIST)	Merck	–
Water for injections (Moscow)	R-pharm	–
Deuterium oxide (D ₂ O) (NIST)	Cambridge Isotopes	99.9%
2,6-Lutidine (2,6-dimethylpyridine) (Moscow)	Merck	0.98+
2,6-Lutidine (2,6-dimethylpyridine) (NIST)	Aldrich	99%+

The chemicals were used as received without further purification

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