

## Aqueous solutions: unusual features

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Unusual features of aqueous solutions (compared to solutions based on other liquids) will be discussed. Three categories will be considered: (i) aqueous solutions of low molecular weight compounds, (ii) aqueous solutions of ionic polymers (polyelectrolytes), and (iii) thermosensitive solutions of water soluble polymers. A common aspect in all three systems is the existence of long-lived mesoscale (larger than atomistic or molecular scale but smaller than macroscopic scale) structures/inhomogeneities that have no direct analogues in systems with other solvents, especially those very different compared to water.

Aqueous solutions of low molecular weight compounds exhibit the presence of mesoscale supramolecular structures (on the order of  $\sim 100\text{nm}$ ). These were evidenced by methods of static and dynamic laser light scattering in a large variety of aqueous solutions of low molecular weight electrolytes, nonelectrolyte compounds, and in aqueous mixtures of liquids [1]. A detailed classification of various systems (including nonaqueous solutions and mixtures) with respect to the capability of formation of the large-scale supramolecular structures was performed (almost hundred of different solute/solvent pairs) and the presence and intensity of the supramolecular organization was correlated with properties and interactions between constituent molecules and ions [2]. Interestingly, it was found that the properties of solvent, not solute, are essential. While the dipole moment of solvent was found as a necessary but not sufficient factor, it was found that the important and critical factor here is the ability of formation of hydrogen bonds between solute and solvent molecules and especially the ability of solvent spatial networking by hydrogen bonding. Kinetics of the formation of these structures upon mixing of water with particular compounds was also investigated, including real-time monitoring [3]. The time scale on which these supramolecular structures develop varies from minutes to weeks, depending on the concrete system. Strictly speaking, emergence of these structures in light scattering data means that there are large regions (objects) with different refractive index compared to the rest of solution. The nature (composition, internal structure) of these objects can be deduced only indirectly by studying, for instance, how these structures respond to external stimuli. Several scenarios will be discussed.

Solutions of ionic polymers (polyelectrolytes) also exhibit the presence of mesoscale supramolecular structures (called polyelectrolyte domains), in spite of the fact that clustering of likely charged polymer chains is counterintuitive at first glance. The presence of domains was found in solutions of tens of different polyelectrolytes and reported in hundreds of papers. Contrary to the above mentioned category of systems, several theoretical approaches were developed to explain the phenomenon, but apparently none of them is currently capable of explaining all experimental findings. A brief outline of our work on this issue will be given [4-6].

Thermosensitive solutions of water soluble polymers represent another category of systems where behavior differs significantly compared to polymer solutions based on other solvents, especially nonpolar aprotic solvents. The critical behavior close to the lower or upper critical solution temperature is very different. While polymers in organic solvents exhibit a diverging (infinitely growing) correlation length upon approaching to the critical temperature leading to a macroscopic phase separation, the same process in water soluble polymers may end on a mesoscopic level. The mesophases reported in literature were found to be stable in a narrow interval of temperatures around the critical one. We will, however, present also our bizarre results where mesophases are stable in a broad temperature range and find also practical use (custom-tailored polymeric nanoparticles with interesting properties) [7,8].

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