



Weak aggregation: State of the art, expectations and open questions



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ABSTRACT

This paper gives an overview of weak aggregation due to long-range molecular forces beyond the first neighbor. Such subtle self-assemblies are an important part of modern colloidal chemistry and concern organic molecules as well as inorganic electrolytes and hybrid aggregates. Diverse aspects of such colloidal aggregations, as described in this special issue, can be characterized by the effective free energy per molecule involved. We discuss here expectations about emerging knowledge in this field and predictive modeling of inorganic as well as organic colloids and hybrid aggregates. Some still open questions are also given.

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1. State of the art

Weak aggregation is an often encountered phenomenon that is related to very small free energies of formation, typically below 1 k_BT per molecule, which corresponds to 2.5 kJ/mole. Such labile structures occur in “Ouzo” emulsions and “pre-Ouzo” microemulsions, stabilized by impurities or antagonistic salts or near a phase boundary, they are also found in flexible membranes and liquid–liquid interfaces, where capillary interactions are relevant, and they can even lead to structured “interphases”.

Many more examples could be given. “Weak self-assembly” can be considered also as the low energy limit of classical micelle and microemulsion formation as well as liquid crystal formation. It governs separation and purification processes and can be important for crystallization processes and nanoparticle formation. It is difficult to optimize liquid product formulations or to understand biological processes without the understanding of weak self-assembly and the related weak, long-ranged interactions between chemical entities or colloidal particles.

Strange enough, weak interactions and weak self-assembly is implicitly used since at least 50 years, but without a solid theoretical background based on first principles [1,2] and the corresponding thorough understanding of their origin. Whereas Gibbs phase rule is of course valid for macroscopic phases, it turns out that subtle local structure transformations within a phase or at phase boundaries crucially influence extraction and purification processes [3,4], and that such phenomena in or out of thermodynamic equilibrium cannot be explained and controlled without the knowledge of weak interactions. We are convinced that the chemistry, biology, and material science of the 21st century must consider such weak interactions, pretty much as the chemistry of the 20th century was dominated by the understanding of covalent interactions.

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Within a phase, pseudo-phases are in constant dynamic equilibrium, as much as real thermodynamic phase equilibria, which means that the chemical potentials of each component must be also the same in each phase or pseudo-phase. Applying this general Gibbs principle for all species in structured fluids together with Gibbs–Duhem equations allows identifying and quantifying the structural origin of weak interactions, as it has been introduced in the case of solubilization in micelles and vesicles by Charles Tanford [5,6].

The most detailed textbook (at masters level) devoted to weak molecular forces beyond the first neighbor and *taking into account a strong entropy term* is probably that by Ken Dill and Sarina Blomberg [7]. A synthesis of a large number of experiments of this enthalpy–entropy cancellation resulting in weak interactions, i.e. <1 k_BT/object has been made recently in COCIS [8,9]. The weak interactions involved in the self-assembly processes described in the present issue are summarized in Table 1.

2. Expectations

Most of the current literature is devoted to “organic” weak aggregates, made from large molecules. The initial questions were coming from Svedberg, who designed the ultra-centrifuge to try to find clear experimental background to distinguish between weak “oligomerization” and proteins as a monodisperse covalently bound polymer (cf. the 1926 Nobel prize lecture of Theodor Svedberg http://www.nobelprize.org/nobel_prizes/chemistry). Eighty years later, careful ultracentrifugation studies evidenced weak aggregation of complex swollen poly-ions, supported by theoretical modeling by Demichelis and coworkers [10]. Some type of equivalent weakly bound “inorganic micelle” or “inorganic collapsed polyelectrolyte” or DOLLOP existed at equilibrium. The story was the same as the one behind the famous sentence “non-sense, Mac Bain”, when he proposed in the 1930s the existence of micelle aggregates

Table 1

Order of magnitude of the weak interaction mechanisms in self-assembled chemical systems and complex colloidal fluids as described in this issue.

Most common name(s) of phenomenon	Colloidal and interfacial mechanism involved	Typical free energy per molecule in aggregate	Author and page numbers in COCIS issue
Preferential adsorption	Enhancing molecular solubilization by preferential adsorption using multi-component solvents	1 to 2 $k_B T$ per hydrophobic solute in the presence of an hydrotrope	D. Horinek This issue 2016;21:X
Ultra-flexible microemulsions	Micromemulsions stabilized by size-dependent hydration and solvent entropy compensation	0.1 to 0.5 $k_B T$ per surfactant	D. Horinek This issue 2016;21:X
Micellar growth beyond the “second cmc”	Chemical potential equilibria between monomers dispersed in a solvent and micelle pseudo-phases	1–2 $k_B T$ per surfactant	M. Bergström This issue 2016;21:X
Stabilization or induction of emulsions of poorly miscible solvents by antagonistic salts	Antagonistic ion separation at a liquid-liquid interface, cosmotropes on the water side and chaotropes on the solvent side	1–2 $k_B T$ per separated ion pair, interacting with solvent molecules at the interface	A. Onuki This issue 2016;21:x
Oxyethylene chain based head-group stabilization	Indirect effect: helical conformation of head-groups induced by water adsorption enhancing contact hydration pressure	Expressed as surface hydration pressure controlling clouding and change of micellar shape	B. Lindman This issue 2016;21:X
Hybrid self-assembly of organic molecules bound by ions	Combination of entropic and polarization effects	Less than 0.5 $k_B T$ of chemical potential variation per surfactant involved	P. Guilbaud COCIS 2015;20:71
Hydration stabilizing interfaces containing a co-solvent	Reference chemical potential step between hydrotrope-rich and hydrotrope-poor phases	0.02 to 0.2 $k_B T$ per hydrotrope or co-solvent molecule	D. Horinek This issue 2016;21:X
Bridging/depletion equilibrium	Bridging combined with depletion; $\Delta\Delta G$ lower than 1 $k_B T$ per aggregate	Exact compensation can result in vanishing free energy difference	L. Sapir This issue 2016;21:X
Surface layering induced by confinement	Fluid density fluctuations induced by hard walls	1–2 $k_B T$ /solvent molecule	K. Nygård This issue 2016;21:X
Hydrophobic effect	Water structuring versus cavity formation	1–2 $k_B T$ / solute; can compensate and vanish	B. Kronberg This issue 2016;21:X W. Ducker This issue 2016;21:X
Ionic aggregates as complex ions or oligomeric DOLLOP	?	?	Expectations and outlook of this paper
Ouzo effect	Chaotic Marangoni turbulence inducing off-equilibrium	Off-equilibrium metastable structures	R. Botet This issue 2016;21:X
Spontaneous emulsification	spontaneous emulsification		
Nanoemulsification due to phase inversion by temperature	Change in spontaneous curvature of interfaces induced by water adsorption/desorption	Temperature cycles not relevant to free energy differences	C. Solans This issue 2016; 21:X

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