



Account/Revue

Organized molecular systems as reaction media

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ABSTRACT

Media are among the most important factors to be considered for organic synthesis in fast and non-polluting conditions satisfying the conditions for sustainable development. Organized Molecular Systems (OMS) are very useful when efforts are being made to apply the twelve green chemistry principles, more precisely to replace organic solvents, to carry out reactions in water, to employ catalysis and biocatalysis, to economize molecules (and, of course, of atoms) and to work with low-energy conditions. These OMS possess a number of advantages: solubilization of substances that are not normally soluble in the continuous phase of OMS, localization of reactants and products, and selective orientation and stabilization of the various entities in the various stages of the reaction. Rapid and selective reactions of preparative amounts of substrate can be carried out in such media, which are also very suitable for mechanistic studies. First, we performed organic photoreactions in microemulsions (macroscopically homogeneous and transparent media). Thus, we were able to confirm the interfacial localization of the processes by means of chemical internal sensors and infrared spectroscopy; to propose a formulation strategy for diminishing the number of substrates in the medium (molecular economy principle); and to use high interfacial concentration to carry out reactions in the liquid phase although they are generally only possible in the solid state. The most important scientific point was the demonstration of the generalization of the amphiphilicity concept, by using polar non-aqueous solvents. 1986 saw the end of a controversy concerning the use of formamide in place of water. With this type of solvent, we have been able to perform important reactions: the Wacker process, Diels-Alder reactions, and olefin amidations. Then we postulated the formation of aggregates without surfactants if differential solvations were operative. All organic reactions can be influenced by the spontaneous formation of aggregates. To finish, with such systems, it is possible to orientate the reactivity of competitive reactions (e.g. cyclization and polymerization) and help to protect the environment, for example in the synthesis of clean surfactants in clean conditions. With the extension of these observations and results to the use of rigid objects (similar to rigid micelles) we were able to obtain very high enantioselective excess in chiral processes.

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1. Introduction

Reactions have been studied in organized molecular media since the 1970s. There is currently much research in this area and the scientific literature on the topic is vast. For example, organic synthesis has been investigated

extensively as reflected in monographs and review articles [1].

In recent years, microemulsions have been shown to be useful as media for a wide range of chemical reactions [2], such as bioorganic synthesis [3], preparation of nanoparticles [4], polymerisation [5], organic synthesis [6], metal-ligand complex formation [7], and enzyme processes [8]. Because the topic is now a mature field of study, it is virtually impossible to cover the entire area of reactivity in organized molecular systems. So this review will

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necessarily be selective and will be mainly focused on the personal work of the authors.

Compared with polar aprotic solvents, such as DMSO, DMF etc. microemulsions are more environmentally benign. Environmentally benign reactions have now become the target of synthetic organic chemists: the development of the concept of green chemistry and its twelve principles acts as a guideline for chemists. It is for this reason that the main objective of this review is to demonstrate that organized molecular systems are very efficient for the application of some of the twelve green chemistry principles, essentially: energy efficiency, safer solvents, atom and molecular economy, less hazardous chemical synthesis, use of renewable feedstocks, catalysis and biocatalysis, enzyme models, and reduced derivatives.

A secondary objective is to emphasize the role of some experimental tools useful for developing research in OMS: generalization of surfactant concepts, utilization of interfacial properties, proximity effects, molecular economy etc.

Organic chemistry has now developed so far that it is time to ask organic chemists about the future of their discipline, and reactivity in organized assemblies is one of the answers to this question [9]. A variety of synthetic reactions have been performed in organized molecular systems (OMS) formed by aggregations of individual molecules [10]. These organized media belong to the new discipline of supramolecular chemistry [11] which may be split into two levels of enquiry:

- level 1: host-guest interactions;
- level 2: study of molecular aggregates.

These both depend on low-energy molecular interactions sharing the following properties: molecular recognition, transport from one phase to another, and catalysis. Organized media, which are employed to facilitate chemical processes, mainly belong to the second level. These media are prepared by dissolving amphiphilic molecules in water or organic solvents. They then self-associate into colloidal entities adopting different forms (micelles, microemulsions, vesicles, etc.). The prime role of water has to be emphasized: defined structures arise spontaneously in water owing to non-covalent forces among the component molecules [12]. They excel as solvents with the further benefit of transparency, which confers particular value in photochemical applications [13]. The interest of such systems lies in their utilization as media for conducting reactions, where the selective dissolution of reactants, the stabilization of species and the bringing together of surfactants all favour catalytic processes. A higher degree of control of chemical reactivity is generally observed, and further progress in the physicochemical comprehension of such systems will undoubtedly help to match structure to reactivity.

2. Choice of system for conducting reactions

In general, organized systems are prepared from hydrophobic solutes, which highlights the important role of water. The solutes belong to four categories:

- surfactants, versatile amphiphilic molecules;
- planar cyclic or heterocyclic compounds which organize themselves in stacks;
- non-planar condensed ring compounds such as sterols, which aid the formation of aggregates with a limited number of components;
- hydrosoluble polymers, which tend to self-associate or organize themselves.

Apart from the systems formed by stacking, which are mainly employed to mimic interactions of purine and pyrimidine bases, media prepared from any of the other solutes can be employed in studies of chemical reactivity. We will discuss only the use of OMS formed with surfactants here.

Surfactants can promote the formation of well-organized monolayers at the various interfaces and aid the formation of aggregates in solution, producing a suspension of microscopic objects. This gives rise to heterogeneous phases within a liquid [14]. In water, spherical or deformed micelles tend to be obtained. According to the concentration and temperature, cylinders and then cubic or hexagonal liquid crystals and, finally, lamellae may be observed (Fig. 1). In non-polar solvents, a different type of aggregate is observed, consisting of reverse micelles which may contain small amounts of water. A number of solvents may be employed instead of water [15]. The degree of organization, however, depends on the cohesion properties (structure) of the liquid (Table 1).

These substitutes may confer benefits from the modification of properties such as polarity and solubility. We have also shown that a protic character is not necessary if the solvent is structured enough (high cohesive energy) and if it has high polarity. 3-methylsydnone is a good example of such liquids. With this mesoionic molecule, we have been able to form all types of aggregates [16] (Table 2).

Owing the low concentration of surfactant necessary to obtain micelles, the quantity of solute in the colloidal medium is very low. Synthesis for preparative purposes necessitates larger quantities, and a microemulsion is the

Table 1
Cohesive solvents.

Solvent	ϵ/ϵ°	μ (D)	γ (mN.m ⁻¹) at 20 °C	DCE (dyne.cm ⁻²) ^a
Water	78	1.8	70	27.5
Glycerol	43	-	63	17.8
Formamide	109	3.4	58	15.0
Ethylene Glycol	38	2.2	48	12.0
N-methyl formamide	182	3.8	35	8.3

^a Density of cohesive energy (DCE) = $\Delta U_{\text{vap}}/\text{Molecular volume} \approx \gamma/(V^{1/3})$.

Table 2
Aprotic structured solvents.

Solvent	ϵ (T°C)	μ (D)	D.C.E. (dyne.cm ⁻²)	γ (mN.m ⁻¹)
3-methylsydnone	144 (40 °C)	7.3	14.0	57 (40 °C)
Formamide	109.5 (25 °C)	3.4	15.0	58 (20 °C)
Water	80 (25 °C)	1.8	27.5	70 (20 °C)

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