

Coacervates as Prebiotic Reactors

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Abstract

In this work we summarize the important findings about coacervates as prebiotic reactors. We have found out that it is possible to run a chemical reaction in a coacervate, which fulfills the early predictions by Oparin that coacervates may have been the original prebiotic reactors. We have prepared two types of coacervates and have found that Passerini reaction in water occurs in both of them.

Introduction and Objectives

Coacervates are important for astrobiology. Specifically, they would be of interest based on the Goal #3, Objectives 3.4, on the “Origins of cellularity and protobiological systems”, from the NASA’s Astrobiology Road Map (<http://astrobiology.arc.nasa.gov/roadmap/g3.html>) (Des Marais et al., 2008). Coacervates are aqueous colloidal systems. They are initially composed of droplets, which eventually equilibrate to form two layers. These are the colloid-rich layer, so-called coacervate, and the colloid-poor layer, known as the equilibrium liquid or supernatant. The two layers, both of which are aqueous, are immiscible (Coacervate, 2011; Creating Coacervates, Flammer web site; Menger and Sykes, 1998).

Prebiotic importance of coacervates was proposed by Oparin in 1924. The typical macromolecular components of Oparin’s coacervates were polypeptides and polysaccharides (Evreinova et al, 1973, 1974, 1975, 1977; Gladilin et al, 1978; Oparin, 1967, 1968, 1969; Oparin and Gladilin, 1980; Walde et al., 1994). The coacervates droplets made from these materials give appearance of amoeba-like objects, which change shape, form “vacuoles”, release “vacuole contents”, flow, merge, divide and show other life-like properties. It should be pointed out that in those early days DNA has not been discovered and that the origin of life was thought to be protein based. Among the most studied features of coacervates is their ability to grow and to mimic self-reproduction, by splitting into the “daughter cells (Creating Coacervates, Flammer web site; Evreinova et al, 1973, 1974, 1975, 1977; Gladilin et al, 1978; Oparin, 1967, 1968, 1969; Oparin and Gladilin, 1980; Walde et al., 1994). According to Oparin, various organic reactions could occur inside coacervates. The coacervates which are able to utilize the organic materials from the environment more efficiently than others would survive better. Thus, a primitive selection could occur which would favor such coacervates. The coacervate systems have been studied also more recently (Burgess 1990; Burgess et al., 1991; Burgess and Singh 1993; Dubin et al., 2008; Liberatore et

al., 2009; Menger 2002, 2011; Menger et al., 2000; Menger and Sykes, 1998; McClements et al., 2009; Rabiskova et al., 1994; Singh and Burgess, 1989; Stuart et al, 1998; Wang et al, 1999, 2000), but not in the prebiotic context.

Results

Our preliminary results were published (Kolb et al., 2012). We give here a summary of our published results and add new findings which we have not published yet.

We have prepared two types of coacervates. The first type was Oparin's and the second one was based on AOT, a surfactant. Oparin's coacervate was prepared by the experimental procedures by Flammer (Creating Coacervates, Flammer web site) and the AOT coacervate by the preparation published by Menger and Sykes (Menger and Sykes, 1998). We show below the structure of the AOT in Fig. 1.

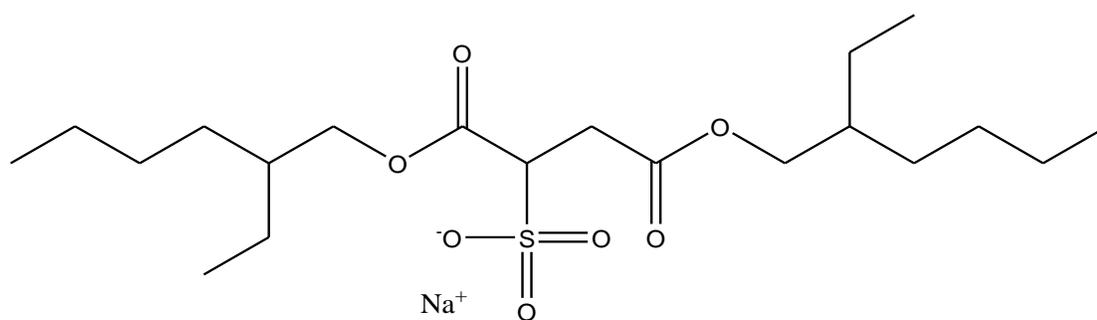


Figure 1. Structure of AOT, Dioctyl sodium sulfosuccinate

The reason why we sought a coacervate different than Oparin's is because polysaccharides which were used in the Oparin's coacervates cannot be prepared prebiotically. In contrast, AOT molecule has all the functional groups and required chemical bonds that have ample precedent in the prebiotic world.

We have chosen Passerini multicomponent reaction (Hooper and DeBoef, 2009) to test the proposal that coacervates could be used as prebiotic reactors. The reasons for this choice are multiple. Firstly, all the components in the Passerini reaction are prebiotically feasible compounds. The same is the case for the product. Secondly, the reactants, although not water soluble, do react in water and they give a single product. Finally, the Passerini reaction has been studied extensively for its pharmaceutical applications. Thus, we could devote our time to running the reaction in coacervates, rather than having to study the reaction nuts and bolts from the beginning. The reaction scheme for the Passerini reaction is shown below, in Fig. 2.

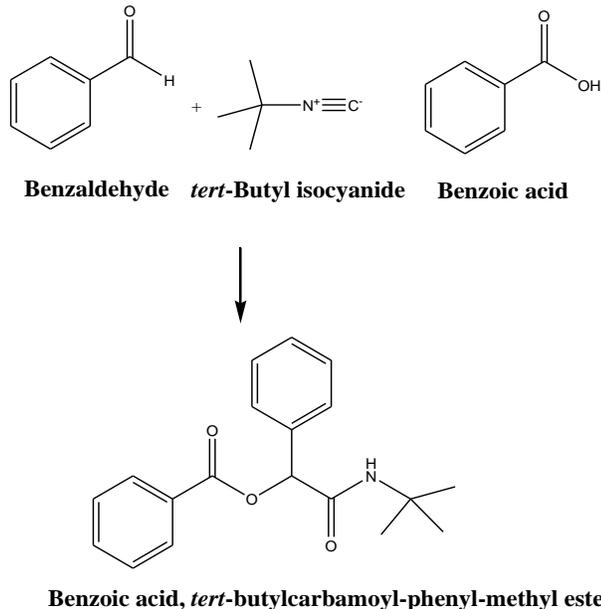


Figure 2. The aqueous Passerini reaction which was used in this study.

The reaction product is a white solid. It was isolated from the coacervate layer, and was washed, dried and analyzed. It is a pure product, which had melting point and IR (Infra-red spectrum) the same as those described in the literature.

The details and procedures of our work are described in our recent publication (Kolb et al., 2012).

Our new and so far unpublished results are concerned with the kinetics of Passerini reaction in the coacervate layer as compared to the equilibrium layer. The research question was if the Passerini reaction will be faster or slower in the coacervate as compared to the equilibrium liquid and pure water. We have obtained preliminary results and the study is in progress. First, we had to slow down the Passerini reaction, since it was too fast already in water, outside the coacervate or equilibrium layer, for us to measure even the relative rates accurately. Addition of additives, such as methanol and salts did slow down the Passerini reaction sufficiently for the measurements to become more reliable. We have added these additives into the Passerini reaction mixture before we transferred it to the coacervate or equilibrium layer. We have prepared coacervates with the same amounts of methanol and salt to match those added to the Passerini reaction mixture. We have improved on the quality of the measurements. We still need to address the fact that AOT and salt are found in the coacervate and equilibrium layer in different concentrations. This is due to the nature of the coacervate preparation. The difference in these concentrations is also expected to be reflected in the rate of the Passerini reaction. We need to measure these differences accurately and set up controls for them in respect to the Passerini reaction. The

preliminary work is described in the Undergraduate Senior Thesis by Armando Ramirez, from UW-Parkside, who has worked in our research group for two semesters.

Acknowledgments

Wisconsin Space Grant Consortium has sponsored this work. UW-Parkside has supported Armando Ramirez via URAP (Undergraduate Research Apprenticeship Program) for two semesters. Both sponsors are gratefully acknowledged.

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