

Experimental study of the effect of system composition on artificial chemotaxis of droplets

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Introduction

Biological chemotaxis is a natural way for cells and organism to move in a chemical gradient (Cejkova, et al. 2017a). Several studies of artificial systems have shown that these systems mimic some properties and behavior of living cells or small living organisms, including chemotaxis. Study of organic droplets as a model of artificial life representing "liquid robots" (Cejkova, et al. 2017b) shows, that organic droplets with the volume of units of microliters floating on aqueous solutions of surfactants can exhibit life-like phenomena such as sensing of chemical signals and responding to them by chemotactic movement.

The behavior of the system most studied in previous work - decanol droplets placed in an aqueous solution of sodium decanoate - is described in detail together with the physicochemical properties of system in (Cejkova, et al. 2014). Experiments have shown that the velocity of droplets is dependent on the concentration of sodium decanoate and also on the type and concentration of added gradient-forming solute. With these acquired information we are able to control the movement of decanol droplets by changing the chemical gradient of solute.

Since we can control the movement of decanol droplets, possibly in the same way we can control other droplets. In present work, we aim to find other systems exhibiting such fascinating phenomena. One of the prerequisites for understanding artificial chemotaxis is the knowledge of interfacial phenomena, so we need to obtain more information about the behavior of different oil droplets on surfaces formed by different solutions of surfactants. The fundamental understanding what are the key properties of the droplet system and what are the proper conditions enabling artificial chemotaxis together with the ability of the droplets to serve as transporters of small objects or chemicals even in complex environments can later open the door to the potential using of droplet systems for environmental cleaning.

Experimental

Chemicals used for the formation of aqueous solutions have been selected in such a way that the created systems are not extremely dangerous to humans, respectively glasses and gloves are sufficient as protective equipment when creating

the system. The second criterion was to use at least one representative from each group of surfactants (anionic, cationic, non-ionic), namely: sodium dodecyl sulfate (SDS), sodium octanoate, cetrimonium bromide (CTAB) and polysorbate 20 (TWEEN 20). Three solutions were formed from each of the surfactants, one of them with a constant concentration of 10mM, the second with a concentration equal to the CMC of the substance, and the third with a concentration 5-10 times lower than the CMC. Specific values of concentrations can be found in Tab. 1.

Surfactant	Solution 1	Solution 2	Solution 3
SDS	10 mM	8.2 mM	1 mM
Sodium octanoate	10 mM	300 mM	50 mM
CTAB	10 mM	1 mM	0.2 mM
TWEEN 20	10 mM	0.06 mM	0.01 mM

Tab. 1: Concentrations of the solutions used in this work.

Alcohols with different hydrocarbon chains - 1-hexanol, 1-octanol and 1-decanol, were used as organic substances for the formation of droplets. Organic dyes (Oil Red O and Sudan Black B) were added to enhance colorless alcohols.

The experimental setup consisted of forming a thin layer of prepared aqueous surfactant solutions on a 76 mm x 25 mm microscope slide. Subsequently, a droplet of 10 μ l alcohol was added to one end of the slide, and the recording of the experiment was started. The whole experiment was captured from above from a video camera, attached to a stand at a height of about 50 cm above the slide.

The main investigated and compared parameters influencing the behavior of systems are surface tension and interfacial tension. These quantities were measured for all solutions on an Attension Theta optical tensiometer.

Results and discussion

The first experiments were performed at a constant surfactant concentration of 10 mM. The behavior of the droplet was mapped for all combinations of surfactant, alcohol from which the droplet was formed, and dye added for highlighting. We found a total of 5 different types of behavior, which will now be described.

	Hexanol			Octanol			Decanol		
TWEEN 20	IV	IV	IV	IV	IV	V	V	V	V
CTAB	I	II	II	II	II	II	IV	IV	IV
SDS	II	II	II	IV	IV	IV	II	II	II
Sodium octanoate	II	II	II	III	III	III	III	III	III

Tab. 2: Types of droplet behavior on specific 10 mM surfactant solutions

Type I: Dissolving the droplet in the solution

Due to the solubility of hexanol in water, we expected this type of behavior for all systems containing hexanol. In our case, however, the solubility is affected by the addition of surfactant and the presence of dye, or there was a stabilization of the droplet due to micelles of surfactant. This type of behavior has been observed in a single system – hexanol droplets without dye on the surface formed by the CTAB solution.

Type II: Disruption of the uniform level

After the alcohol drops onto the surface of the solution, the uniform layer of the aqueous solution is torn into two or more parts, at the point where the alcohol droplet is added, the aqueous solution recedes to the edges (Craster and Matar, 2007). This phenomenon can also be associated with the tearing of the droplet itself into several small droplets, which subsequently, if they still have a sufficiently large volume, continue to expel the surfactant solution.

Type III: Movement of the droplet to the edge of the slide

For systems with a large difference in surface tension between solution and droplet, in this case sodium octanoate solution ($\gamma = 65.08 \text{ mN.m}^{-1}$), the droplet tries to reach the edge of the slide, where it remains indefinitely due to its significantly lower surface tension. However, unlike other systems, the layer does not tear with a droplet.

Type IV: Movement of the droplet due to division

This type of system is characterized by the division of the droplet into several smaller ones, either immediately after dripping on the surface of the solution, or after a certain characteristic time, which differs for individual systems. The division takes place by one of two mechanisms - the first of which is characterized by a change in shape and subsequent tearing (Caschera, et al. 2013). The second method is a sudden increase in the surface of the droplet several times and its subsequent shrinkage, during which a few small droplets are released. This type of separation is often followed by dissolving these droplets in solution, as a larger droplet is insoluble in solution because the solution would be supersaturated at some point.

Type V: Spontaneous movement of a droplet on a slide

These systems are characterized by repeated movement from one side of the slide to the other, due to the slow gradual dissolution of the droplet causing movement behind the fresh or least contaminated surfactant (Toyota, et al. 2009). Unlike other systems, this type of behavior makes it possible to describe its trajectory and velocity due to the existence of a single droplet.

Only in one case was found a similarity with the system sodium decanoate - decanol - salt in the way that it would be possible to measure the speed and direction of chemotactic

movement depending on the type and concentration of added chemicals. Observed phenomena such as droplet dissolution or micelle formation are undesirable for finding systems exhibiting artificial chemotaxis. Therefore, the following experiments were performed only with decanol, whose solubility in water is negligible, and the critical micellar concentrations of individual surfactants were also considered in order to eliminate the phenomena caused by micelles on the surface, as you can see in Tab 1.

The main idea of the following experiments was to maintain the same ratio of surfactant concentration to CMC as the 10 mM sodium decanoate solution has to its CMC. The CMC for sodium decanoate is around 80 mM for 25°C, and therefore the solutions of surfactants used in this work were chosen at a concentration 5-10 times lower than the critical micellar concentration.

This fact is reflected in relatively high values of interfacial tension in comparison with interfacial tension of sodium decanoate. A typical behavior for systems with lower surface tensions than the surface tension of the decanol droplet was the movement of the droplet to the meniscus at the edge of the slide, where after contact with the slide, it began to push away the applied aqueous solution. The same behavior was observed for solutions with high values of surface and interfacial tension. In this case, however, the liquid layer was not disturbed.

For future work, the most interesting are those systems in which the droplet has moved for some time, but after a certain time has stabilized in one place, which means that the response to the addition of dissolved chemicals to the system can be measured. These systems had a very similar interfacial tension to sodium decanoate, but the necessary condition is that the solution has a higher surface tension than an oil droplet.

Conclusion

We tested several dozen systems differing in the type and concentration of surfactant, the length of the hydrocarbon chain of the alcohol forming the droplet and the presence of the dye. Thanks to the obtained information about surface energies and system behavior, we are able to predict the requirements for systems that could be suitable for the study of chemotaxis, namely: 1) surfactant concentration should not exceed CMC to eliminate micelle effects; 2) oil droplet should have as much the lowest solubility so that its dissolution does not create the gradient needed for movement; 3) the interfacial tension between the droplet and the solution should be very low (around 4 mN/m); 4) the surface tension of the solution must be higher than the surface tension of the droplet. In the following work we will focus on such systems in order to describe in more detail the mechanism of artificial chemotaxis.

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