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Review

Spontaneous formation of vesicles

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Abstract

This review highlights the relevant issues of spontaneous formation of vesicles. Both the common characteristics and the differences between liposomes and vesicles are given. The basic concept of the molecular packing parameter as a precondition of vesicles formation is discussed in terms of geometrical factors, including the volume and critical length of the amphiphile hydrocarbon chain. According to theoretical considerations, the formation of vesicles occurs in the systems with packing parameters between 1/2 and 1.

Using common as well as new methods of vesicle preparation, a variety of structures is described, and their nomenclature is given. With respect to sizes, shapes and inner structures, vesicles structures can be formed as a result of self-organisation of curved bilayers into unilamellar and multilamellar closed soft particles. Small, large and giant uni-, oligo-, or multilamellar vesicles can be distinguished. Techniques for determination of the structure and properties of vesicles are described as visual observations by optical and electron microscopy as well as the scattering techniques, notably dynamic light scattering, small angle X-ray and neutron scattering. Some theoretical aspects are described in short, viz., the scattering and the inverse scattering problem, angular and time dependence of the scattering intensity, the principles of indirect Fourier transformation, and the determination of electron density of the system by deconvolution of $p(r)$ function. Spontaneous formation of vesicles was mainly investigated in catanionic mixtures. A number of references are given in the review.

Keywords: Catanionic mixtures; Liposomes; Mixed systems; Packing parameters; Scattering techniques; Spontaneous vesicle formation; Vesicles

Contents

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1. Introduction

1.1. Historical aspects of liposomes and vesicles

Because of their chemical structure, surface-active substances, amphiphiles, show the ability of self-organisation in the solvents, forming self-assemblies with a large variety of morphologically different structures [1]. The phase behaviour of surfactant systems and their corresponding static structures have been most studied. However, the morphological dynamics of these processes is not only of fundamental interest, but it plays an important role in many technological applications. Several products rely on their colloidal, chemical, microencapsulating and surface properties; these products range from drug-dosage forms (antifungals, anticancer agents, vaccines) and cosmetic formulations (skin-care products, shampoos) to diagnostics and various uses in the food industry, etc. [2–10]. Knowledge about the dynamics of formation, and the structure of aggregates, makes it possible to control further processes [11]. Properties of the system depend strongly on sample preparation. Morphological transitions in surfactant systems can be triggered by a large variety of parameters, e.g., by mixing processes, dilution, changes in the solution composition, or chemical reaction, and by changes in either temperature or pressure [12,13]. However, morphological transitions may also be induced by applying external fields such as shear, electric or magnetic fields. In order to gain a full understanding of either the morphology of the initial structure or the appearance of a newly formed one, appropriate experimental techniques provide sufficiently detailed structural information. Common methods are typically either direct visualisation (optical or electron microscopy) or scattering techniques (light scattering, LS, small angle neutron scattering, SANS, small angle X-ray scattering, SAXS).

In this review, the methods of vesicles preparation, spontaneous formation of catanionic vesicles, and the methods for structural observations will be described.

Some facts about liposomes and vesicles have to be emphasised; the difference is due to the chemical composition of amphiphilic molecules. Liposomes are formed from phospholipid molecules and are called lipid vesicles, sometimes simply vesicles; they are supramolecular assemblies of amphiphiles that contain two hydrophilic tails and one hydrophobic head group. Other vesicles, lamellar bilayers and multilayers are formed from different surfactants.

The discovery of liposomes is attributed to A.D. Bangham, who performed research on blood and blood clots in 1961, particularly on the colloid behaviour of lecithin and other phospholipids. He found that phospholipids form spheres in the diluted aqueous solutions [14]. Citing Bangham's paper, these spheres were described as, "Liposomes are the smallest artificial vesicles of spherical shape that can be produced from natural nontoxic phospholipids and cholesterol. Liposomes are microscopic, fluid-filled pouches whose walls are made of layers of phospholipids identical to the phospholipids that make up cell membranes." The appearance and permeability of the phospholipids membranes were similar to the properties of biological membranes. For that reason, liposome research was used as the model for biological membranes. Liposomes are characterised by their size, the number of layers, and by their surface charge. According to the surface charge sign, they are classified as anionic, cationic and neutral liposomes. Although the discovery of lipid vesicles in the early 1960s was made by Bangham, papers about the colloid behaviour of lecithin and other phospholipids can be found much earlier. In 1811, Vauquelin described the bonding of phosphorus onto the fatty acids within the material isolated from the brain using hot ethanol [15]. Cylindrical structures that were growing very fast from thin layers exhibiting nice colours under crossed polarisers were investigated. In that research, lipids extracted from brain tissue were mostly used. Firstly, their structures and shapes were observed from dried myelin material that Lehman named myelin figures [15]. Gobley described the presence of a lipid substance in the chick brain containing phosphorus similar to that present in the egg yolk [16]. Lehmann investigated patterns by polarisation microscopy; today, these patterns are called big multilamellar vesicles [17]. Mechanical stress as well as crystal defects caused some of the cylinders to grow, and being detached from the original lipid material, they closed the outer angles forming suspended colloid particles—liposomes.

Introduction of the electron microscope, more than a hundred years later, made it possible to understand that those particles are closed structures containing in their inner part a liquid that can diffuse freely. Former experiments claimed that