Colloids and Surfaces A 558 (2018) 1–7

Contents lists available at ScienceDirect

Colloids and Surfaces A

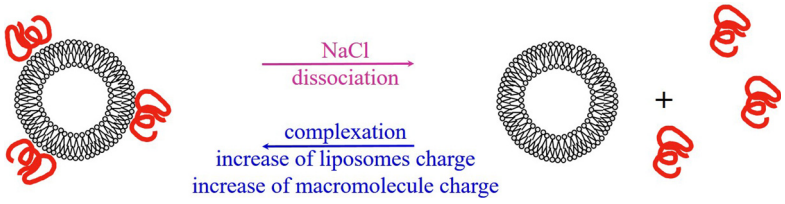
journal homepage: www.elsevier.com/locate/colsurfa

Stabilization of electrostatic polymer-colloid complexes

Alexander A. Yaroslavov, Andrey V. Sybachin*, Anna A. Efimova

Chemistry Department, Lomonosov Moscow State University, Leninskie Gory, 1-3, Moscow, 199991, Russia

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Liposomes
Polyelectrolytes
Interfacial complex
Stability
Adsorption
Reversibility

ABSTRACT

A series of copolymers with a constant degree of polymerization (600) and a molar fraction of cationic units, α, varied from 0.4 to 0.96, were electrostatically bound to liposomes, 40–60 nm diameter, with a molar fraction of anionic lipid, ν, varied from 0.1 to 0.4. The properties of the resulting complexes were analyzed with the following main conclusions. The complexation induces concentration of all anionic lipids, initially uniformly distributed within the membrane, on the outer membrane leaflet. The dissociation of the electrostatic liposome-polycation complexes is controlled by a concentration of salt in the surrounding solution. Adjusting the α and ν values allows to control the NaCl concentration which ensures a complete dissociation of the liposome-polycation complex. The stability of electrostatic liposome-polymer complex in aqueous-salt solutions is interpreted in terms of the force between the two nano-sized plates: an anionic liposomal membrane and a cationic polymer adsorbed over the membrane ("separated charges concept"). This approach can be useful for controlling the complexation/dissociation for biomedical application, catalysis, diagnostics, etc.

1. Introduction

Adsorption of polymers with ionic groups, polyelectrolytes, on the oppositely charged substrates (glass, metal, polymer, clay) is a simple and effective way for surface modification [1–4]. This technique allows to render desirable functionality to the surface [5,6], tie proteins and small compounds onto the modified surface [7], protect the surface from exposure to environment [8,9], cover the surface with a thin bactericidal film [10,11], facilitate (expedite) purification procedures of products [12,13]. With use of alternative adsorption of cationic and anionic polyelectrolytes, multilayer coverings with controllable thickness can be constructed that retain stable within wide limits of salt concentrations and pH values [14–16]. Polyelectrolyte binding to the surface of colloidal particles stabilizes them against aggregation [17,18] improves mechanical properties of soft colloids (micelles, lipid vesicles and microgels) [19,20] increases adsorption capacity of colloidal particles to ions and small substances [21] allows vectorial modification of colloidal drug carries and diagnostic agents [22,23]. The kinetics and mechanism of the polyelectrolyte adsorption has been extensively investigated for many years; the results are summarized in numerous reviews, see Refs. [24–27]. for the recent. Among various factors controlling capacity of substrates to ionic polymers and stability of the resulting interfacial layers in aqueous salt solutions, a total charge on the macromolecule and charge density on the surface were expectedly found to play key roles [24]. In the majority of cases, only one parameter was varied – the surface charge density or polymer

* Corresponding author.
E-mail address: sybatchin@mail.ru (A.V. Sybachin).

https://doi.org/10.1016/j.colsurfa.2018.08.042
Received 21 June 2018; Received in revised form 6 August 2018; Accepted 15 August 2018
Available online 23 August 2018
0927-7757/ © 2018 Elsevier B.V. All rights reserved.

structure, and the polymer adsorption was mainly controlled by experimental or theoretical study [28,29]. A few examples can be mentioned where properties of both surface and polymer as well as adsorption/desorption equilibrium are discussed [30,31]. The restrictions resulted from difficulties with controllable surface modification [32,33] and methods for monitoring adsorption/desorption events [34–36].

Spherical bilayer lipid vesicles (liposomes) are a perspective object for quantification of the polyelectrolyte adsorption/desorption. Liposomes with a desirable content of the surface anionic groups can be easily prepared by a simple mixing of anionic and zwitter-ionic (electroneutral) lipids at a specific lipid-to-lipid ratio [37]. Small anionic liposomes, from 40 up 60 nm in diameter, have been shown to adsorb cationic polymers electrostatically [38,39] no additional “anchoring”, for example via a hydrophobic contact, is observed [40]. Adsorbed polycations are completely removed from the liposome surface when a simple salt is added to surrounding solution [41]. Finally, the liposome surface can be easily made fluorescent via incorporation of a small amount of a fluorescent-labeled lipid into to the lipid mixture during liposome preparation [42]. Since polycations are effective fluorescence quenchers, a decrease and further recovery of fluorescence reflect adsorption/desorption processes in the anionic liposome-polycation binary system [43].

Recent investigations have demonstrated the dependence of strength of electrostatic interactions between polyelectrolytes and opposite charged liposomes i.e. concentration of simple salt needed for the complete dissociation of polymer/liposome complexes, upon molar fraction of charged lipid in membrane [44]. This result is quite unusual and unexpected taking into account the fact that interfacial complexes of flexible polyelectrolyte/liposome represent themselves individual macromolecule adsorbed on cluster of segregated opposite charged lipids [39–41,44]. Increase of charged lipid molar fraction in membrane results in increase of number of macromolecule/lipid domain complexes in one liposome [40]. So one could expect negligible change of critical salt concentration inducing complex dissociation or even no change in this critical concentration as it was demonstrated for interpolyelectrolyte and electrostatic polymer/micelles complexes [45–49]. The interpretation of the phenomena was given from the analysis of the experimental data and computer simulations [29,41]. However, up to now the concept of stability of polyelectrolyte/liposome complex suffers from the absence of analyzing the role of macromolecule charge. The study of polyelectrolyte/liposome complex stability when varying the degree of polymerization of macromolecules might clarify the organization of interfacial complexes [39,42].

The aim of this research is to evaluate the role of the charge of components in polycation/anionic liposome complexes on their stability towards dissociation in water-salt media. The interpretation of the experimental data will be helpful in analyzing structure and properties of macro-objects formed by separated multicharged surfaces.

2. Materials and methods

2.1. Materials

Small unilamellar anionic liposomes, composed of anionic 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (PS) with melting temperature (T_m) of 14 °C (Fig. 1a) and egg yolk lecithin (EL) which is a mixture of zwitter-ionic lipids with T_m below 0 °C (Fig. 1b), both from *Avanti Polar Lipids*, were prepared by the standard sonication procedure [43]. The details on lipid composition could be found in Supplementary Material. A molar fraction of anionic PS lipid calculated as ν = [PS]/([PS] + [EL]) was equal to 0.1, 0.2, 0.3 and 0.4. The concentration of the freshly prepared stock suspension of the liposomes was 10 mg/mL. Dynamic light scattering (with cumulant analysis procedure) showed size of liposomes fluctuated within 40–60 nm interval with average PDI of 0.243; no correlation between size fluctuation and PS content was observed. EPM of liposomes became more negative with increasing a ν value: from −1.20 to −2.40 (μm/c)/(V/cm) (see Fig. 2a). No change in liposome size and EPM was detected within daytime of experiment, 5–8 h.

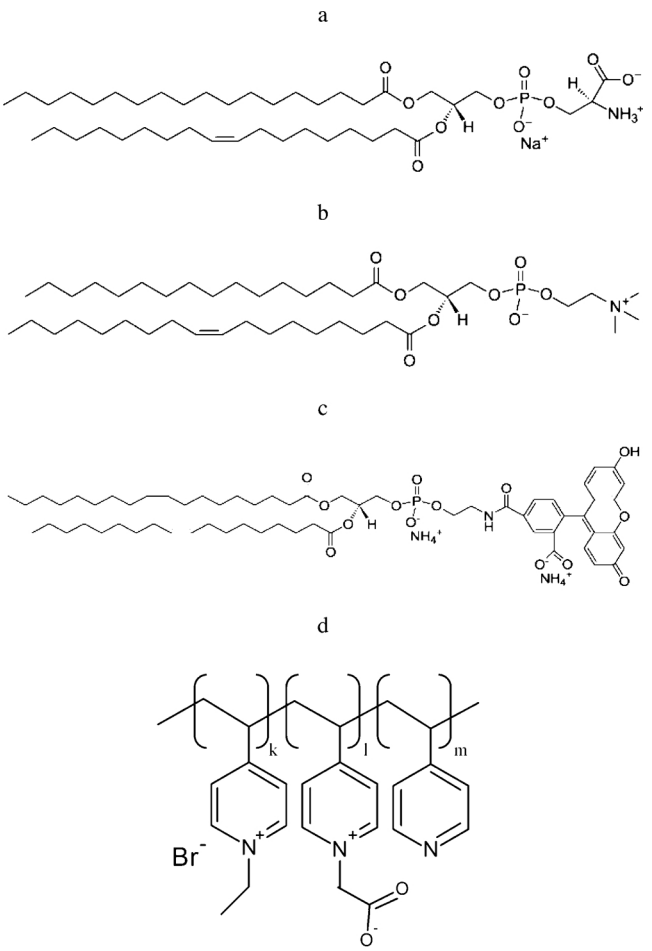


Fig. 1. Phosphatidylserine (a), egg yolk lecithin – representative structure (b), dioleoylphosphoethanolamine-*N*-carboxyfluorescein ammonium salt (c), polymers (d).

Liposomes with a fluorescent dye incorporated into the membrane were prepared by the same procedure, except 0.1 wt% of dioleoylphosphoethanolamine-*N*-carboxyfluorescein ammonium salt (PE-CF) (Fig. 1c) from *Avanti Polar Lipids* was added to the lipid mixture solution before chloroform evaporation. Unless otherwise specified, liposome solutions with 1 mg/mL lipid comcentration were used.

Polymers were obtained via alkylation of poly(4-vinylpyridine) with DP 600 (*Aldrich*) by alkyl bromide and bromoacetic acid and characterized as described elsewhere [42] (Fig. 1d). A molar fraction of cationic (quaternized with ethyl bromide) pyridinium units in the copolymers, α, varied from 0.96 to 0.4 while the fraction of zwitter-ionic (quaternized with bromoacetic acid) pyridinium units in the copolymers, β, varied from 0.21 to 0.56 and the fraction of the residual non-quaternized units, γ, from 0.03 to 0.94 (Table 1). Concentrations of copolymers are represented in moles of cationic pyridinium units per liter, [P^+].

Each liposome-polymer sample was prepared via mixing of a liposome suspension and a polymer solution.

2.2. Methods

The fluorescence intensity of CF-labeled liposome suspensions was

Download English Version:

https://daneshyari.com/en/article/8954004

Download Persian Version:

https://daneshyari.com/article/8954004

Daneshyari.com