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Electrostriction of supported lipid films at presence of cationic surfactants, surfactant–DNA and DNA–Mg^{2+} complexes

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Abstract

The method of electrostriction has been applied to study the physical properties of supported lipid membranes (sBLM) during membrane formation at application of negative potential. Application of negative potential −350 mV to the sBLM during its formation resulted in more compact membrane structure as revealed by higher elastic modulus in comparison with sBLM formed without application of this potential. We also studied interaction with sBLM cationic surfactant hexadecylamine (HDA), HDA–DNA and DNA–Mg^{2+} complexes. Interaction of HDA with sBLM resulted in decrease of membrane capacitance and two-directional effect on elasticity modulus (increase or decrease), which can be caused by different aggregation state of surfactant at the surface of sBLM. In contrast with effect of HDA, the complexes of HDA–DNA resulted, in most cases, increase of elasticity modulus and increase of membrane capacitance, which can be caused by incorporation of these complexes into the hydrophobic interior of the membrane. Certain part of these complexes can, however, be adsorbed on the sBLM surface. DNA itself does not cause substantial changes of physical properties of sBLM; however, addition of bivalent cations Mg^{2+} to the electrolyte-contained DNA caused substantial increase of elasticity modulus and surface potential. These changes are, however, much slower than that observed for HDA–DNA complexes, which can be caused by slow competitive exchange between Na^{+} and Mg^{2+} ions.

Keywords: Electrostriction; Capacitance; Cationic surfactants; Surfactant–DNA complexes; DNA–Mg^{2+}–lipid complexes

1. Introduction

The study of the mechanisms of DNA–lipid interactions has an important role for understanding the processes connected with gene expression [1] and electroporation of DNA through plasmatic membranes of the cell [2]. Because DNA is negatively charged, it does not induce substantial changes of physical properties of the membranes itself, but only at presence of cations, like Ca^{2+} or Mg^{2+}. At the presence of these cations, so-called triple complexes are formed [1]. Also, the transfer of DNA into the cell is more effective when nucleic acid is in complexes with cationic lipids [3], cationic antibiotic [4] or cationic surfactants [5].

It has been shown that DNA, at presence of bivalent cations, induces shift of phase transition of saturated phosphatidylcholines toward higher temperatures. This effect has been explained by partial denaturation of DNA at the lipid bilayer surface, which makes possible interaction of bases with hydrophobic part of the membrane [3]. Recently performed ultrasound velocimetry study of DNA–DPPC interactions at the presence of calcium ions showed induction of biphasic stage of the melting curves, which has been explained by coexistence of the free lipids and the strongly bound one [6]. DNA interacts with cationic surfactants cooperatively, as has been shown recently by Petrov et al. [5]. These authors found different effects of cationic surfactants—dodecylamine (DDA) and dodecyltrimethylammonium bromide (DTAB) on secondary structure of DNA. While DTAB stabilized DNA structure, DDA resulted in its destabilization. The destabilizing effect of DDA has been explained by means of the displacement of intramolecular hydrogen bonds in complementary base pairs with intermolecular H-bonds between unsubstituted DDA amino groups and proton-accepting sites of nucleic bases. Existence of DNA–lipid interaction has been revealed also by increased

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surface pressure of lipid monolayers following addition of plasmid DNA [2]. DNA can also interact with positively charged peptides [7,8].

Despite extensive study of DNA–lipid interactions, only little is known about mechanisms of these processes. The effect of DNA and DNA–cationic surfactant complexes on membrane electrostriction has not been studied yet. This work is therefore concerned with the study of the effect of cationic surfactant hexadecylamine (HDA), DNA–HDA complexes and DNA at presence of Mg^{2+} ions on the electrostriction of supported lipid membranes (sBLM). We should note, however, that the abbreviation sBLM is commonly used despite the fact that the structure of these membranes formed on the tip of cut wire is not exactly bilayer.

2. Experimental

2.1. Chemicals

DNA from calf thymus was purchased from Sigma (USA). It has been fragmented by mild sonication in bath sonicator for 75 s resulting in formation of fragments with length of about 200–3500 base pairs as has been determined by gel electrophoresis. DNA has been diluted in concentration of 3.3 mM in buffer: 10 mM HEPES (pH 7.6) containing 10 mM NaCl as has been determined spectrophotometrically. The DNA concentration is presented in terms of nucleotides. The stock solution was stored frozen. Cationic surfactant hexadecylamine (HDA) (Sigma) was used for formation of DNA–surfactant complexes from stock solution contained 3.3 mM HDA dissolved in buffer with 10 mM DNA, which corresponded to the molar ratio HDA/DNA = 1:1. At certain concentration, the HDA forms micelles in water. This so-called critical micellar concentration (cmc) has been determined by turbidimetry and for HDA was 2.75 mM. Lipid membranes were formed from soybean phosphatidylcholine (SBPC) (P-l Biochemical, USA) dissolved in *n*-decane (Fluka, Switzerland) in concentration 50 mg/ml.

2.2. Formation of supported lipid membranes (sBLM)

sBLM have been formed on the tip of freshly cut silver wire (diameter 0.5 mm) according to the method by Tien and Salamon [9]. The wire was coated by insulating polymer film formed by electropolymerization according to Ref. [10]. During the formation of sBLM in buffer, the negative potential −350 mV was applied to the sBLM relative to the reference Ag/AgCl electrode according to Haas et al. [11], which improved the covering of the wire by lipid film. Lipid bilayers formed from SBPC were negatively charged as has been revealed by measurement of surface charge density [12].

2.3. Measurement of elasticity modulus, $E_\perp$, coefficient of dynamic viscosity, η, electrical capacitance, C, and surface potential, Φ, of sBLM

The electrostriction method allows us the simultaneous measurement of the Young's modulus of elasticity in direction perpendicular to the membrane plane, $E_\perp$, coefficient of dynamic viscosity, η, membrane capacitance, C, and surface potential, Φ. These values were measured by applying an ac voltage (amplitude $U_0 = 50$ mV and frequency $f = 1$ kHz) to the sBLM. Membrane capacitance is given by

$$C = I_1/2\pi f U_0 \quad (1)$$

where I_1 is the amplitude of the 90° component of the first current harmonic. The modulus of elasticity perpendicular to the membrane surface, $E_\perp$, is given by

$$E_\perp = -p/(\Delta d/d) \quad (2)$$

where $\Delta d/d$ is the relative change in membrane thickness resulting from the application of pressure p. In our setup, this pressure results from the applied ac voltage (electrostriction), and induces a time-dependent change of the bilayer thickness reflected in a third harmonic component of the current (amplitude I_3; see Refs. [13,14]). Using $p = C_S U_0^2/2d$ for the electrostrictive pressure, where C_S is the specific BLM capacitance per unit area, the Young's modulus can be calculated from

$$E_\perp = C_S U_0^2 I_1/4dI_3 \quad (3)$$

For this calculation, we used C_S, determined from electrical capacitance of BLM which contained *n*-decane: $C_S = 0.37$ μF/cm^2. The thickness was determined from equation: $d = \varepsilon\varepsilon_0/C_S = 5$ nm, where $\varepsilon = 2.1$ is relative dielectric permittivity of the hydrophobic part of the lipid film and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is dielectric permittivity of vacuum (see Ref. [13]). The values of C_S and h were then corrected to the real values, corresponding to the hydrophobic part of lipid films (see Section 3.1). The coefficient of dynamic viscosity can be estimated by the following equation [13]:

$$\eta = (E_\perp \sin\varphi)/2\pi f \quad (4)$$

where φ is the phase shift between pressure and membrane deformation and f is the frequency of deformation.

Two different sources of potentials are present in the system: electrode potentials, U_{el}, and surface potentials of the membrane, Φ. The surface potential consists, in general, of Gouy–Chapman surface charge potential (U_{GC}) and surface dipole potential (U_D):

$$\Phi = U_{GC} + U_D \quad (5)$$

The changes in intrinsic potential can be determined using equation [13]

$$\Phi = -U_1 + U_0 I_2/4I_3 \quad (6)$$

where I_2 is the amplitude of the second harmonic of the membrane current with frequency $2f$, which is generated if the membrane is compressed simultaneously both by ac and dc voltages. U_1 is dc voltage externally applied to the BLM. The method of measurement of Φ is based on simultaneous determination of the amplitudes of the current harmonics I_2 and I_3 (see Ref. [13]).

For a classical BLM separating two aqueous phases, the electrode potentials can generally be closely matched, making their net contribution in the total circuit very small. With metal-supported membranes, there is an inherent asymmetry in the electrode materials (stainless steel or silver wire vs. calomel electrode) and environments (lipid vs. aqueous phase). Thus, the electrode potentials on the two sides of the bilayer may be quite different, and cannot be determined easily. Similarly, the different environments at the two faces of the BLM will introduce further asymmetry into the system. Both configurations of the head group layer in contact with the metal support, and the electrical interaction with the support (e.g., mirror charges) will differ from the situation at the aqueous boundary [14]. For agar-supported membranes, however, this asymmetry is rather small and is mostly determined by salt concentration in agar bridge and in aqueous solution.

Measurements of the electrical parameters were carried out at apparatus described in detail elsewhere [13] under the control of an IBM PC/AT 286 computer and were done at $T = 20$ °C. For measurement, the alternating voltage with relative small amplitude (50 mV) with a frequency of 1 kHz was applied to sBLM. Additional dc potential (− 350 mV) necessary for membrane formation was applied to sBLM from computer-controlled D/A transducer.

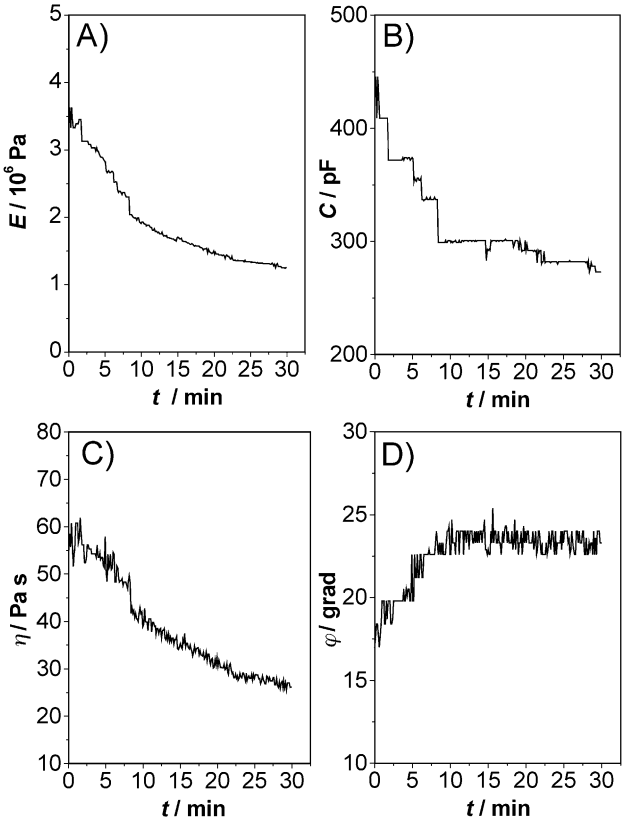

Fig. 1. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, (B) membrane capacitance, C, (C) coefficient of dynamic viscosity, η, (D) phase shift, φ, of sBLM formed at the tip of freshly cut Ag wire following application of negative potential (− 350 mV) vs. Ag/AgCl electrode (negative terminal is on the Ag wire). sBLM were from soybean phosphatidylcholine dissolved in n-decane (50 mg/ml).

3. Results and discussion

3.1. Formation of sBLM

Haas et al. [11] showed that formation of sBLM under application of negative potential is accompanied by decrease of electrical current and membrane capacitance. This has been explained by decrease of the structure defect in lipid film due to formation of multilayer lipid structure at the hydrophobic surface of the silver. Similar effect has also been observed in this work. In addition to the membrane capacitance, we measured also changes in elasticity modulus and phase shift. The values of elasticity modulus and phase shift have been used for calculation of the coefficient of dynamic viscosity according to Eq. (4). These values are plotted in Fig. 1 as a function of time. We can see that all values decrease with time, except for the phase shift. As we mentioned, analogical decrease of membrane capacitance has also been observed in paper by Haas et al. [11]. In this work, the final steady state value of capacitance has been in the range 170–210 pF. The average capacitance obtained in our experiments was 194 ± 36.5 pF (mean ± S.E. obtained from independent experiments on 16 membranes). Larger average values obtained in our experiments are due to larger diameter of the wire: 0.5 mm, instead of 0.38 mm used in Ref. [11]. The average capacitance values obtained in present works correspond to the thickness of hydrophobic part of lipid film: $d = 18.5 \pm 3.5$ nm ($d = \varepsilon\varepsilon_0 A/C$, where $\varepsilon \approx 2.1$ is the relative dielectric permittivity of the hydrophobic part of the membrane, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the dielectric permittivity of free space and A is the membrane area). Considering that the hydrophobic part of lipid bilayer containing n-decane has thickness approximately 5 nm [13], it is possible to conclude that lipid film at the metal support has multilayer structure. This conclusion is in agreement with that reported by Haas et al. [11]. The estimation of film thickness, however, did not take into account the thick inhomogeneities and edge part of sBLM. Therefore, the real value of the film area should be less than that calculated on the base of wire diameter, and hence, the film thickness should also be lower than that presented above. Fig. 1 shows that both elasticity modulus and coefficient of dynamic viscosity decrease, and phase shift increases with time (i.e. under continuous application of the voltage − 350 mV at the sBLM). At the calculation of elasticity modulus and

coefficient of dynamic viscosity according to Eqs. (3) and (4), it has been assumed that sBLM has bilayer structure. However, decrease of membrane capacitance evidences that the corrections on "true" value of capacitance and thickness are necessary in order to obtain real value of elasticity modulus, $E'_{\perp}$, and coefficient of dynamic viscosity, η':

$$E'_{\perp} = E'_{\perp}(I_{10}/I_1)^2 \quad (7)$$

$$\eta' = \eta(I_{10}/I_1)^2 \quad (8)$$

where the I_{10} is the amplitude of first current harmonics at $t=0$. The corrected values of both $E'_{\perp}$ and η' are presented in Fig. 2 together with uncorrected one, i.e. $E_{\perp}$ and η. We can see that corrected values revealed considerable less changes with time and after approximately 30 min of application of negative potential of sBLM, the steady state values have been obtained. We should note that while decrease of membrane capacitance following application of negative potential has been obtained in 15 cases from 16 independent membranes tested (in 1 case, no changes of capacitance took place), for elasticity modulus, the decrease was obtained in 9 cases, its increase was observed at 4 cases, and at 3 cases, no changes took place. Certain variations in direction of changes of elasticity modulus can be due to inhomogeneity of the membranes that contain huge number of solvent molecules (i.e. *n*-decane) that in addition can form microlenses.

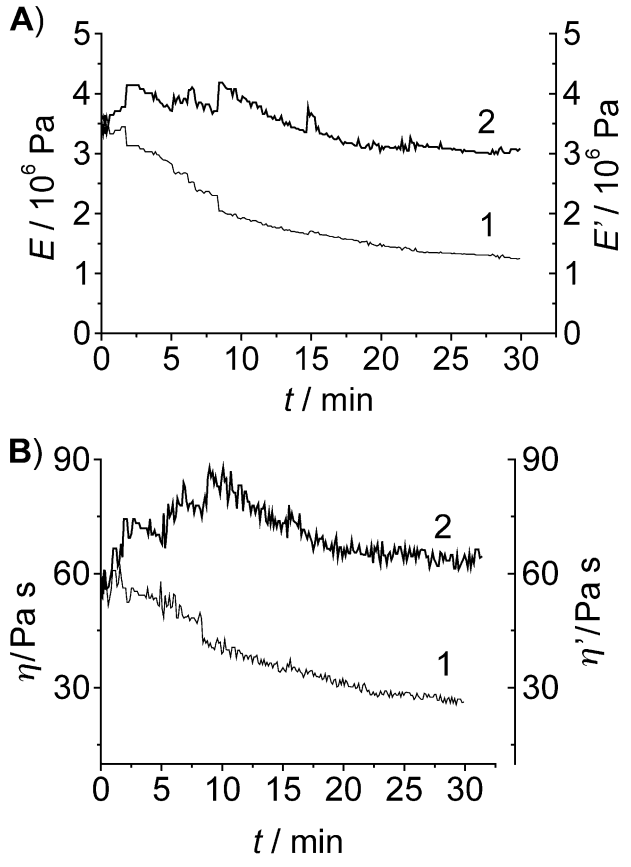

Fig. 2. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$ (1) and that corrected on increased thickness of the membrane, $E'_{\perp}$ (2) according to Eq. (7); (B) the same for coefficient of dynamic viscosity, η (1) and that corrected on increased thickness of membrane, η' (2) according to Eq. (8).

It is interesting to compare behavior of sBLM formed under application of negative potential and that formed at open circuit potential [15]. In the latter case, the formation of sBLM was accompanied by increase of membrane capacitance and decrease of elasticity modulus. It has been shown by Passechnik et al. [15] that these sBLM (i.e. formed without application of negative potential) are unstable in time. The changes of their electrical and mechanical parameters are due to the formation of islands of uncovered metal parts (which are characterized by considerable higher capacitance due to formation of double electric layers of cations in a close distance from metal surface) and inhomogeneities caused by solvent redistribution. The inhomogeneities that contained the solvent are more compressible than the ordered parts of lipid bilayers. The elasticity moduli of these membranes were $(1.6 \pm 1.2) \times 10^6$ Pa, while for sBLM of the same composition, but formed under application of negative potential, 2.5 times larger values were observed: $(4.12 \pm 2.34) \times 10^6$ Pa.

Thus, application of negative voltage during formation of sBLM resulted in formation of compact lipid layer at the metal surface, which is more ordered in comparison with sBLM formed at open circuit potential.

3.2. Interaction of HDA with sBLM

Hexadecylamine (HDA) is a molecule composed of amino group and hydrophobic chain. The amino group is positively charged at neutral pH. At low concentration, the HDA is in the form of monomer, while above critical micellar concentration (2.75 mM) forms micelles. In this section, we will present results on the study of the interaction of HDA with stabilized sBLM, i.e. formed under application of negative potential. The sBLM were kept at this potential approximately 30 min. Then only alternating potential of relatively small amplitude (50 mV) with a frequency $f=1$ kHz was applied to the membrane in order to measure changes of the physical properties of sBLM.

After the steady state values of capacitance and elasticity modulus have been obtained, the HDA was added into the buffer at the final concentration of 0.1–1 mM from stock solution of HDA (10 mM). In most cases, the HDA at lower concentration (up to 0.3 mM) did not cause changes of membrane capacitance and elasticity modulus. However, at higher concentration, addition of this surfactant resulted in increase of elasticity modulus and decrease of membrane capacitance (Fig. 3). Relative changes of these values as a function of HDA concentration are presented in Fig. 4. We can see that the shape of these changes is sigmoidal, which may evidence about certain cooperativity of interaction of HDA with sBLM. Probably the accumulation of HDA

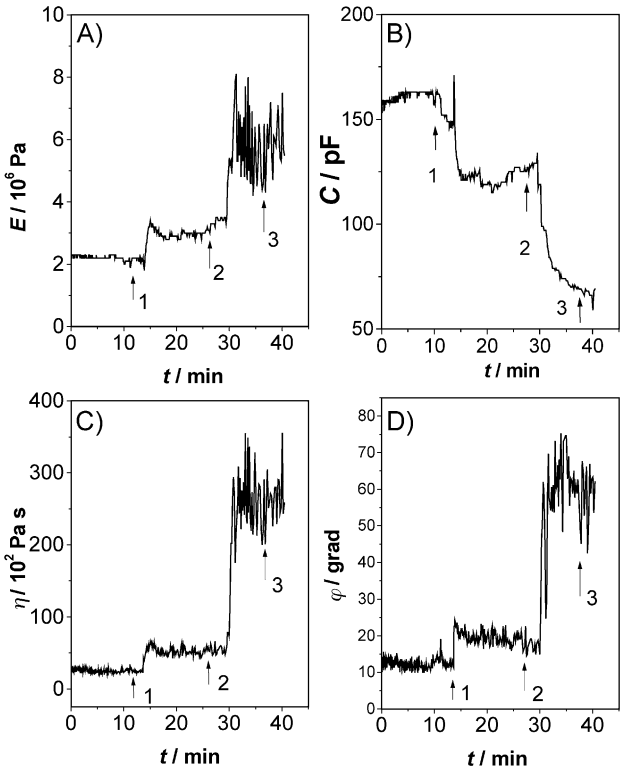

Fig. 3. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, (B) electrical capacitance, C, (C) coefficient of dynamic viscosity, η, and (D) phase shift, φ following addition of hexadecylamine (HDA) at concentrations of 1—38 μM, 2—56 μM and 3—75 μM. Moment of addition of HDA is showed by arrows.

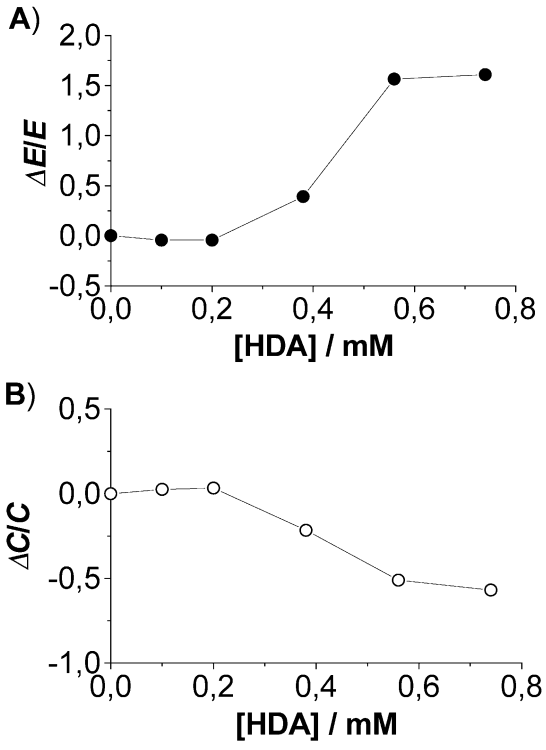

Fig. 4. The relative changes of (A) elasticity modulus, $E_{\perp}$, and (B) membrane capacitance, C, of sBLM as a function of concentration of HDA.

monomers at the membrane surface resulted from higher concentration formation of aggregates, which is more efficient to change the properties of sBLM in comparison with monomers [16]. We should, however, note that the changes of physical properties of sBLM following addition of HDA below the critical micellar concentration were not very reproducible. At certain cases, we observed increase of elasticity modulus and decrease of membrane capacitance already at lower concentrations (0.1 mM). At some cases, addition of HDA at concentration 0.1 mM resulted in increase of elasticity modulus without substantial changes of membrane capacitance. Then for c>0.3 mM HDA, the elasticity modulus and capacitance decreased (Fig. 5).

Different changes of the values of $E_{\perp}$ and C following addition of HDA can be particularly explained by different aggregation state of surfactant at the surface of lipid film. Surfactant can be both in monomeric or micellar state (Fig. 6). Incorporation of monomers into the bilayer could result in decrease of free volume in the lipid layer, and electrostatic attractive forces also increase the ordering of the polar part of the sBLM. These two effects should explain increase of elasticity modulus. The formation of micelles, on the other side, could cause appearance of additional

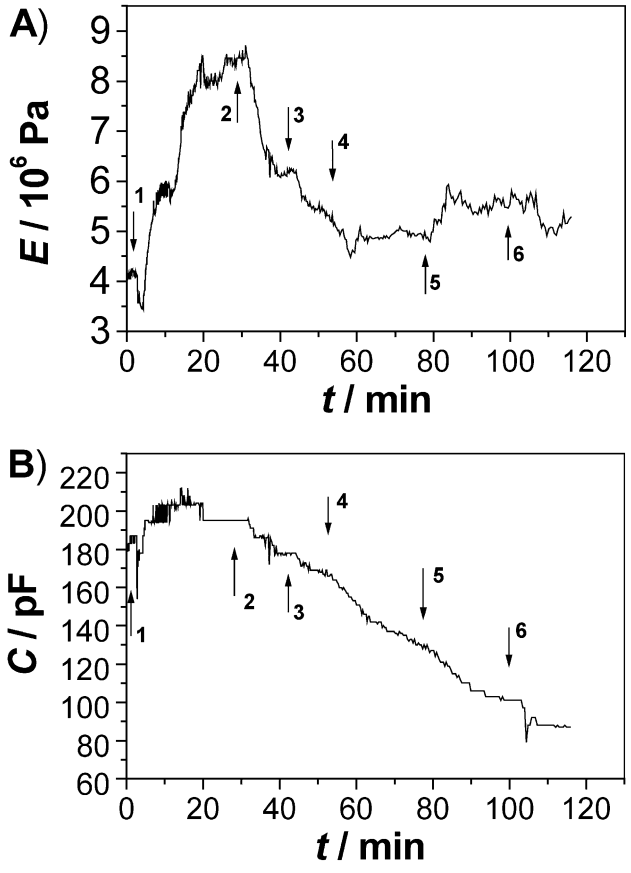

Fig. 5. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, and (B) electrical capacitance, C, following addition of hexadecylamine (HDA) at concentrations of 1—10 μM, 2—20 μM, 3—29 μM, 4—38 μM, 5—65 μM and 6—100 μM. Moment of addition of HDA is showed by arrows.

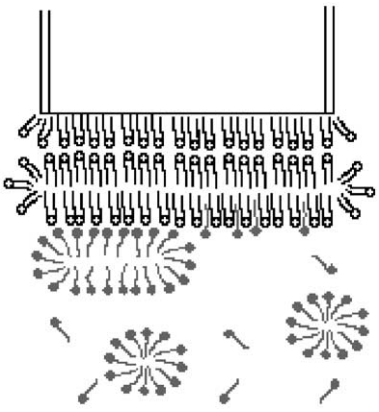

Fig. 6. Schematic representation of HDA monomers and micelles at the surface of sBLM.

layers at the sBLM surface and thus decreases membrane capacitance. The layers of HDA could also contribute to overall elasticity modulus of the sBLM. Considering that elasticity modulus, $E_{\perp}$, of BLM composed of diacylphosphatidylcholines (e.g., SBPC) is higher than that for a-monoglycerides (i.e. molecules composed of one hydrophobic chain), we should expect that the decrease of elasticity modulus could be due to both lower elasticity modulus of HDA layers as well as the increased number of layers at the surface of sBLM (see the effect of increased thickness of sBLM on $E_{\perp}$ value discussed in Section 3.1). We should note that different directions of changes of elasticity modulus at the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB) or neutral surfactant Triton X-100 have been reported in our earlier work. We showed that the changes of physical properties of BLM also depended on the initial state of the elasticity modulus of the membrane (see Ref. [13]).

3.3. Interaction of the HDA–DNA with sBLM

Due to the electrostatic interactions between positively charged amino groups of HDA and negatively charged phosphate groups of DNA, the complexes of HDA–DNA are formed [5,17,18]. The interaction of complexes (HDA/DNA = 1:1 mol/mol) with sBLM was studied by measuring elasticity modulus, membrane capacitance and surface potential following addition of complexes into the buffer from stock solution, where complexes were at concentration of 3.3. mM. Interaction of complexes with sBLM resulted in different changes of the values $E_{\perp}$, C and Φ. In Fig. 7, we can see typical kinetic changes observed following addition of the complexes: increase of elasticity modulus, membrane capacitance and surface potential. The changes of relative values of these parameters are showed in Fig. 8. However, at certain cases, after initial increase of elasticity modulus and membrane capacitance, decrease of these values was also observed at higher concentration of complexes (not shown).

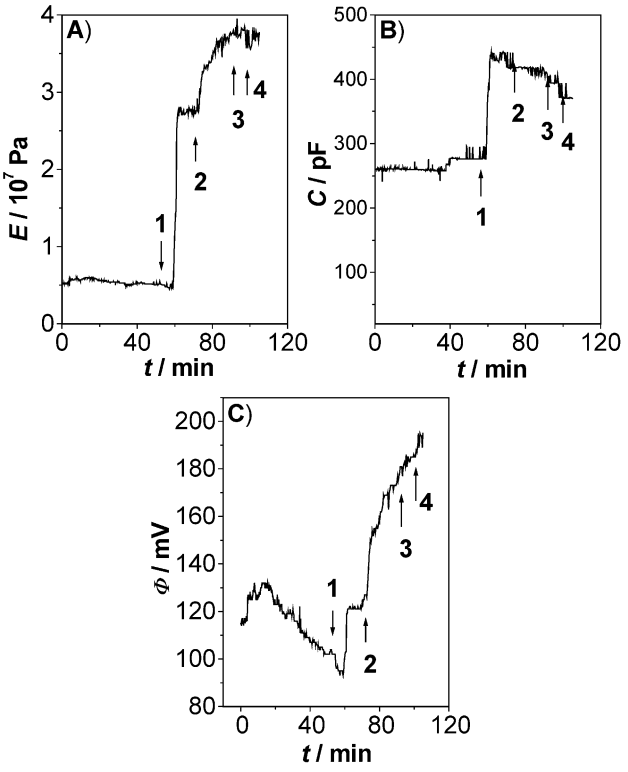

Fig. 7. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, (B) electrical capacitance, C, and (C) surface potential, Φ, of sBLM following addition of the complexes HDA–DNA at concentrations of 1—300 μM, 2—400 μM, 3—500 μM and 4—550 μM. Moment of addition is showed by arrows.

Considering the obtained results, two types of processes could be suggested to explain observed changes of physical properties of sBLM following adsorption of the complexes HDA–DNA. (1) The complex could be incorporated into the sBLM (see Fig. 9), which could be accompanied by increase of relative dielectric permittivity of the hydrophobic part of the lipid layer and, consequently, to the

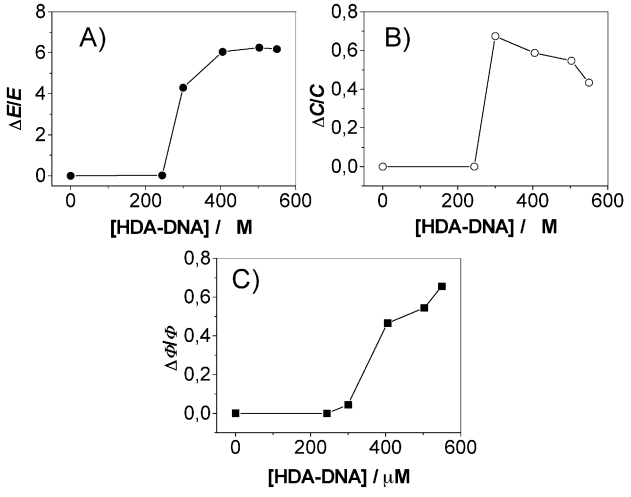

Fig. 8. The relative changes of (A) elasticity modulus, $E_{\perp}$, (B) membrane capacitance, C, and (C) surface potential, Φ, of sBLM as a function of concentration of HDA–DNA complexes.

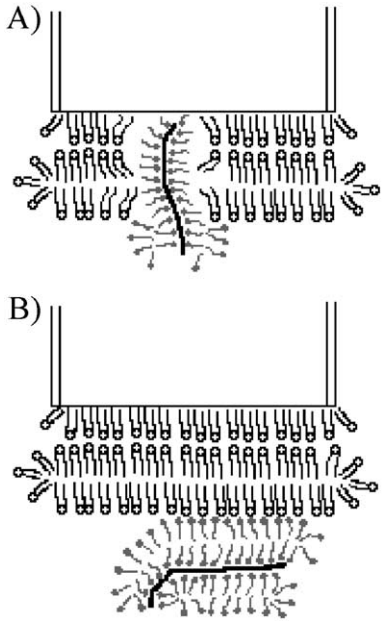

Fig. 9. Schematic representation of the interaction of HDA–DNA complexes with sBLM. (A) Complex HDA–DNA is incorporated into the lipid film; (B) complex is adsorbed at the surface of lipid film.

increase of membrane capacitance. The increase of membrane capacitance can be, however, also caused by structural defects in lipid layers that can be induced by HDA–DNA interactions. (2) At certain cases, the increase of elasticity modulus was observed, but capacitance did not change. This effect can be explained by incorporation of monomers of HDA into the lipid layer. These monomers are not involved into the formation of HDA–DNA complexes. (3) Adsorption of the complexes could result to increase of sBLM thickness (Fig. 9), which was observed at certain cases as a decrease of membrane capacitance.

Thus, we can see that HDA and HDA–DNA complexes caused different effects on sBLM physical properties. While interaction of HDA with sBLM was in all cases accompanied by decrease of membrane capacitance, the interaction of complexes resulted also to capacitance increase or did not induce changes of this value at simultaneous increase of elasticity modulus. The obtained results clearly evidence that the complexes of HDA–DNA are not only adsorbed on the membrane surface but could be incorporated into the lipid interior and/or could induce changes in the hydrophobic part of the lipid membrane. We should, however, note that observed differences could be particularly caused by changes in

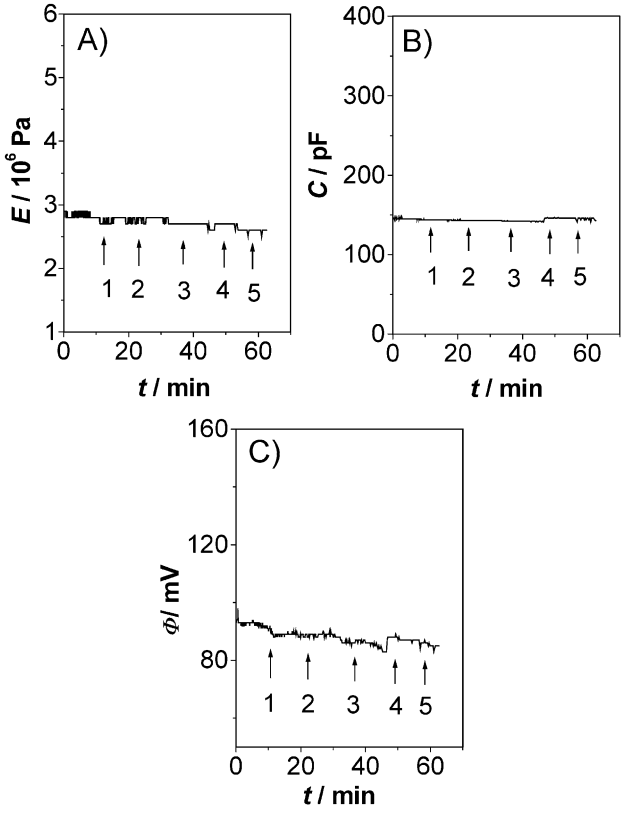

Fig. 10. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, (B) membrane capacitance, C, and (C) surface potential, Φ, of sBLM following addition of DNA into the electrolyte contained 10 mM NaCl at different final concentrations of 1—0.065 mM, 2—0.19 mM, 3—0.3 mM, 4—0.4 and 5—0.52 mM. The moment of addition of DNA is showed by arrows.

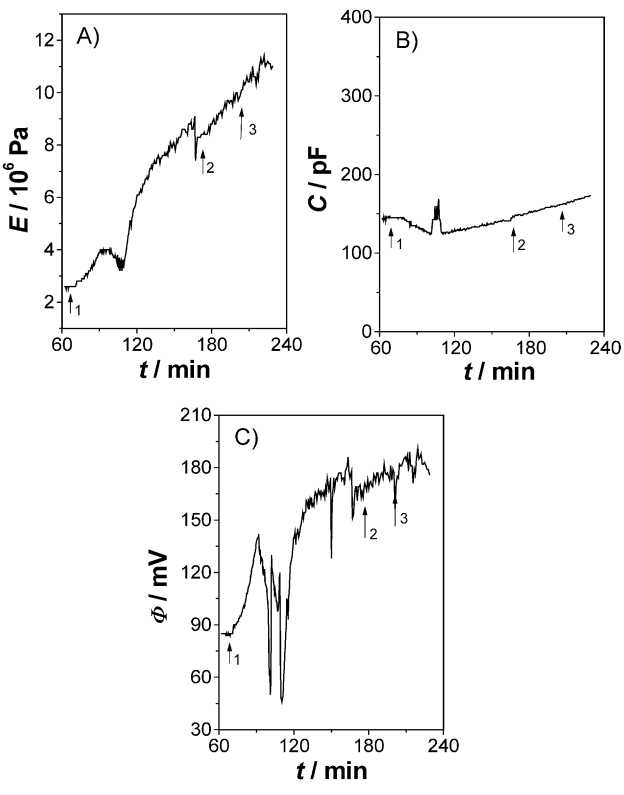

Fig. 11. The kinetics of changes of (A) elasticity modulus, $E_{\perp}$, (B) membrane capacitance, C, and (C) surface potential, Φ, of sBLM following addition of Mg^{2+} into the electrolyte contained 10 mM NaCl and 0.52 mM of DNA. Mg^{2+} was added in final concentrations of 1—3.8 mM, 2—5.6 mM and 3—7.4 mM. The moment of addition of Mg^{2+} is showed by arrows.

the process of micelle formation at presence of DNA as has been recently showed by Sukhorukov et al. [19]. They showed that two different DNA–surfactant complexes are formed at presence of DNA and that the cmc for surfactants was 15–40 times lower than that without DNA. It has been assumed that amphiphile molecules act as linkers, which favor DNA aggregation.

3.4. Interaction of the complexes DNA with sBLM—influence of Mg^{2+}

At the first series of experiments, we studied interaction of DNA with sBLM without Mg^{2+} ions. In this case, addition of DNA into the buffer at concentration range 21–170 μg/ml did not result to any substantial changes of elasticity modulus, membrane capacitance and surface potential (Fig. 10). This means that negatively charged DNA cannot adsorb to the negatively charged surface of sBLM at sufficiently close distance in order to induce the changes of membrane physical properties.

Substantial changes of sBLM properties have been observed when Mg^{2+} has been added into the electrolyte where DNA was present at concentration 170 μg/ml (0.52 mM). This is seen in Fig. 11. Addition of Mg^{2+} at relatively low concentration (up to 7.5 mM) resulted in substantial increase of elasticity modulus, increase of surface potential and modest changes of electrical capacitance. It is interesting that we observed changes of physical properties of sBLM at lower concentration of Mg^{2+} than that characteristic for triple complexes (DNA–Mg^{2+}–phospholipid) reported earlier for liposomes [1]. We should note that Mg^{2+} itself (without DNA) did not induce changes of sBLM physical properties. This is also in agreement with result obtained by Haas et al. [11]. In this work, the authors did not observe changes of membrane capacitance at presence of 1 mM concentration of Mg^{2+}.

Increase of elasticity modulus and surface potential clearly evidences the formation of the complexes DNA–Mg^{2+}–lipid head groups at the surface of sBLM. This binding by means of the Mg^{2+} cations probably resulted in restriction of the mobility of phospholipids and consequently could result in increase of the ordering of lipid layer. Small increase of elasticity modulus following addition of bivalent cations could be caused with competitive binding of Na^{+} and Mg^{2+} ions to DNA. At the first moment, the DNA molecules are surrounded by Na^{+} ions. These ions are, however, not able to mediate interaction of DNA with membrane. Addition of Mg^{2+} resulted in adsorption of these ions to the negatively charged surface of sBLM and they also start to compete with Na^{+} to bind with DNA. This competitive binding could be one of the possible reasons of slow process of binding DNA to the membrane. Comparison of the speed of changes of physical properties of sBLM induced by DNA–Mg^{2+} complexes is really much slower than that induced by HDA–DNA complexes. While in the former case, the changes last several tens of minutes, at the latter case, they are less than 1 min.

4. Conclusion

Application of negative potential to the solid-supported membrane during its formation resulted in more compact membrane structure as revealed by higher elastic modulus in comparison with sBLM formed without application of this potential. Interaction of cationic surfactant, hexadecylamine (HDA), with sBLM resulted in decrease of membrane capacitance and induced two-directional change of elasticity modulus (increase or decrease), which can be caused by different aggregation state of surfactant at the surface of sBLM. In contrast, the complexes of HDA–DNA resulted, in most cases, increase of elasticity modulus and increase of membrane capacitance, which can be caused by incorporation of these complexes into the hydrophobic interior of sBLM. Certain part of these complexes can, however, remain adsorbed on the sBLM surface. DNA itself does not cause substantial changes of physical properties of sBLM; however, addition of bivalent cations Mg^{2+} to the electrolyte caused substantial increase of elasticity modulus and membrane potential. These changes are, however, much slower than that for HDA–DNA complexes, which can be caused by slow competitive exchange between Na^{+} and Mg^{2+} ions.

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