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Impedimetric response of phospholipid Langmuir-Blodgett films to methanol vapors

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Aimed chemical biosensor applications, we have experimentally studied the electrical impedimetric response of Langmuir-Blodgett (LB) nano-thin monomolecular films of phospholipid dipalmitoyl-phosphatidyl-ethanolamine (DPPE) to methanol vapors. DPPE LB films were deposited on planar interdigital electrodes. The ability of such sensing element based on LB films with a thickness of about 3 nm to detect methanol vapors at ambient temperature was estimated by measurements with electrochemical impedance spectroscopy in the frequency range 0.1 Hz – 100 KHz of the applied electric field. DPPE LB films were exposed to methanol vapors at concentrations in the range from 80 to 320 mg/dm^3. Being in contact with methanol vapors, a significant decrease in the surface resistance of the studied LB films was observed. This effect was reversible. The results also showed a clear change in dielectric properties of the DPPE LB films affected by methanol vapors.

Keywords: electrochemical impedance spectroscopy (EIS); gas detection; Langmuir-Blodgett films; methanol vapors; phospholipids.

INTRODUCTION

Methanol is widely used in various industries (organic synthesis, pharmaceutical and plastics industry) for the production of e.g. dyes, drugs, detergents, pesticides, explosives. Methanol is a toxic compound, in particular by inhalation of its vapors and can injure the eyes. Furthermore, the methanol vapors are flammable and explosive. That is why the detection of the presence of methanol vapors is very important for protection of both human health and the environment. For detection of methanol and for safety purpose, various methods can be used. Most of the high-performance analytical methods currently used, e.g. gas chromatography or mass spectroscopy, are laboratory methods for measurement and thorough analyses. More desirable option is the use of an appropriate sensor because of the possibility of quick measurement in the place of potential threat. Among the large variety of sensor elements, micro-devices and systems for chemical sensing, are those based on films prepared by Langmuir-Blodgett (LB) technique [1–7]. In particular, LB films have been employed as active layers for gas sensing [8], including surface-acoustic-wave resonator (SAWR) sensors for methanol vapors [9]. The application of lipid LB films to design biosensors for harmful gases is of research and practical interest. In this direction, besides the optical methods, appropriate and advantageous is the use of electrochemical impedance spectroscopy technique (EIS) as an electrical method of detection.

The employment of interdigitated array electrodes is promising for bio- and chemical sensor applications because in this case the detection sensitivity becomes much higher than the sensing by use of conventional configuration of two metallic electrodes [10–14]. Such microelectrode arrays are very suitable for gas sensor and biosensor applications, and for construction of micro-sensor devices owing to their simple structural design and ease of fabrication [10, 15]. Interdigitated microelectrodes and EIS have been used as chemical sensors and to identify odors [11, 16]. Very recently, a measuring technique using surface acoustic-wave resonators and gravimetric method for detection were successfully applied to assess the impact of vapors of several volatile organic compounds on LB films of phospholipid dipalmitoyl-phosphatidyl-ethanolamine (DPPE) deposited on interdigitated microelectrode arrays [17]. In particular, the influence of the adsorbed methanol on the properties of such mass-sensitive sensor element was studied [17]. In the present work, we tested DPPE LB nano-thin LB molecular monolayers deposited on interdigitated microelectrodes to detect and quantify methanol vapors by means of EIS. DPPE molecule is appropriate and promising for biosensor applications owing to the two long hydrocarbon tails with 15 CH_2 groups each (Fig. 1a) that may provide excellent adsorption of some gases (such as methanol) with possible high sensitivity by sensor applications.

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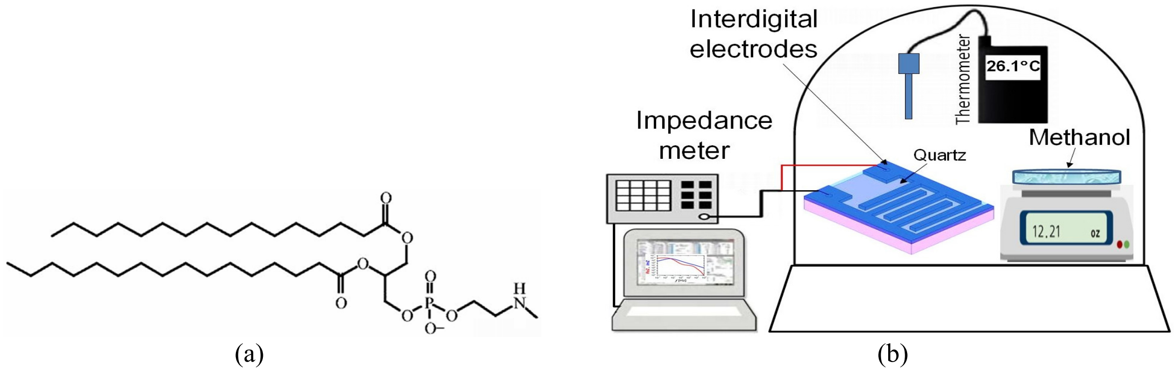

Fig. 1. (a) Chemical structure of DPPE; (b) a sketch of the experimental set-up.

EXPERIMENTAL

LB molecular monolayer of phospholipid DPPE with a nanometer thickness [17] was deposited on the surface area of patterned planar interdigitated gold microelectrodes. For the purpose, microelectrode array structure of SAWR [17, 18] was used. The substrate material of SAWR was quartz. The mean thickness of the studied DPPE LB films was estimated to be about 3 nm according to the measurements by small-angle X-ray diffraction (similar to those described in [19]), as well as measured with atomic force microscopy [17, 18]. The use of interdigitatal electrodes (two metallic electrodes in a comb shape, Fig. 1b) aims at considerably enhanced sensitivity of the electrical detection. In our case, they had a height (thickness) of 100 nm and a width of 1.7 µm, the electrode spacing (separation gap) was 1.7 µm (Fig. 1a). The other technical parameters and the topology of the planar interdigitated microelectrode array are given in details in [20]. EIS combined with similar microelectrode structures is advantageous for electrical sensing [10, 15].

The experimental set-up used in the present work is illustrated in Fig. 1(b). The examined gas detector element, composed of DPPE LB film deposited on interdigitated microelectrodes was placed inside a glass exicator and connected to an electrical impedance-meter (outside the exicator). Liquid methanol in a Petri dish was evaporated at constant temperature in the exicator. The concentration of methanol vapor in the exicator volume was varied from 80 to 320 mg/dm^3. The vapor concentration was determined by measurement of the weight loss of the liquid methanol in the dish by means of sensitive electronic balance. The experiments were conducted after temperature stabilization of the exicator. During the measurements, the temperature was kept fixed at 26 ± 0.1 °C, outside as well as inside the exicator. A sensitive thermo-couple inside the exicator was used as a reference sensor interfaced to an electronic device for additional control of the interior temperature in the measurement chamber.

The electrical impedimetric behavior of the DPPE LB molecular monolayer upon exposure to methanol vapors was studied by EIS technique in the frequency range 0.1 Hz – 100 kHz. This range was selected because no clearly observable effect of methanol vapors on the impedances was observed at frequency above 100 kHz in our tests under the present experimental conditions. EIS measurements were performed at room temperature, with an electrical impedance meter SP–200 (BioLogic Science Instruments, France) controlled by a computer. The frequency spectra of complex electrical impedance in the plane of the LB film were recorded at AC sinusoidal probe voltage of amplitude 1 V (RMS). The measurements were performed in a grounded Faraday cage to avoid the interference of the external field strength with the measured electrical signal.

RESULTS AND DISCUSSION

By EIS technique [21–23], the raw experimental data - both real and imaginary parts of the complex electrical impedance, *ReZ* and *ImZ*, respectively, were simultaneously measured as a function of the frequency *f* of the AC electric field applied on the sample. Fig. 2 presents the frequency spectra of *ReZ* and *ImZ* measured for the studied DPPE LB film exposed to methanol vapors at various concentrations. It can be seen that in the presence of methanol vapors, the impedance values of the DPPE LB monolayer may greatly decrease. By gradually increasing concentration of methanol vapors, gradually reduced impedances are registered in the low-frequency region of the spectra. The effect is more clearly pronounced for *ImZ* spectra. It is well known that the decrease in *ReZ*(*f*) and *ImZ*(*f*) values toward the zero frequency is related to the decrease of the Ohmic resistance and the electrical capacitance, respectively [21–23]. By dielectric in capacitor-like geometry, the decrease in *ReZ*(*f*) and *ImZ*(*f*) values toward the zero frequency is caused by the electrode polarization (EP) effect. At low frequencies, this process dominates over the other dielectric polarization processes. EP is an accumulation of long-distance traveled charges at the interfaces between the electrode and the dielectric film. The strong contribution of EP could be expected by the interdigital microelectrode arrays like the configuration used in this work.

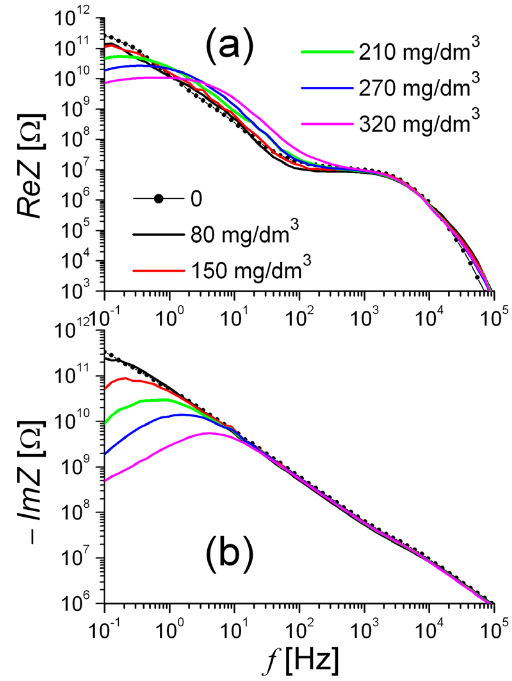

Fig. 2. Frequency spectra of real *ReZ* (a) and imaginary *ImZ* (b) parts of complex electrical impedances measured for DPPE LB film deposited on interdigital electrodes, being exposed to methanol vapors. The concentrations (mg/dm^3) of the vapors are given; 0 corresponds to methanol gas-free case. The temperature was 26 °C.

The observed changes of the impedance behavior were reproducible and reversible – by removal of methanol both *ReZ* and *ImZ* impedances return to the spectra corresponding to the initial vapors-free case. Because of considerable methanol gas-induced change, the impedimetric response of the examined DPPE LB films can be used for detection of methanol in gas phase.

Fig. 3 shows the Nyquist plots (-*ImZ versus ReZ*) for the DPPE LB film. The depressed semicircles in the high to medium frequency regions of the analyzed frequency range in these complex impedance diagrams point out an electrical conduction process [21–23]. The conduction can be attributed to the adsorption of the methanol gas molecules on the surface of the DPPE LB film. The adsorption of methanol gas molecules on the surface of the DPPE LB film deposited on interdigital microelectrodes was evidenced by a gravimetric method of detection where the mass of the adsorbed gas is directly measured [17, 18]. The mechanism of interaction between methanol gas molecules and phospholipid DPPE LB molecular monolayer is rather complicated because of the competition between the rates of adsorption and desorption of the gas molecules. Generally, the stable detection of methanol vapors by the considered DPPE LB films should be achieved at the equilibrium of the rates of adsorption and desorption (the equilibrium is hard to be described by mathematical equations).

In our case, the adsorption of the methanol gas molecules on the surface of the phospholipid DPPE LB film is assisted by the electrostatic interactions at the surface or near the surface [24, 25] of the phospholipidic LB film, namely electric dipole-dipole intermolecular interactions between the polar head of phospholipid DPPE molecular structure and the dipolar methanol molecules. As known, the permanent electric dipole moment of methanol molecule in the gas phase at room temperature is 1.7 D. As a result, an increase of the concentration of adsorbed methanol gas molecules leads to a strong effect on the electrical impedances of the DPPE LB molecular monolayer, expressed in an increase of its electrical surface conductivity.

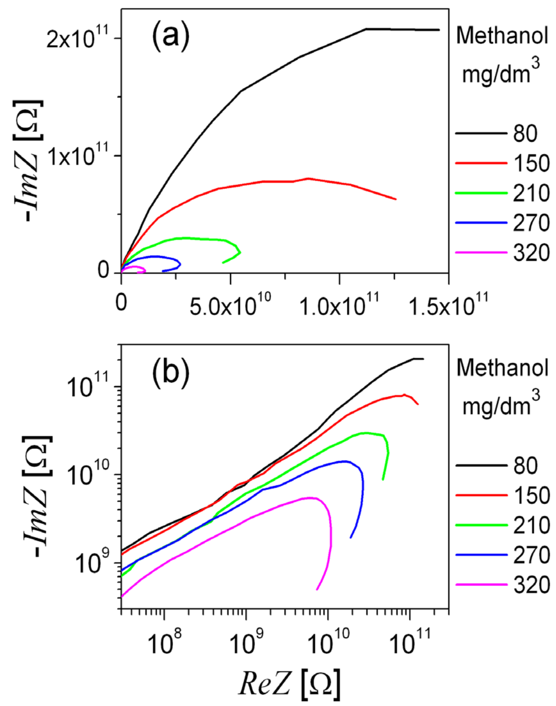

Fig. 3. Nyquist plots for complex electrical impedance measured for DPPE LB film exposed to

methanol vapors at various concentrations: (a) and (b) are the plots in linear and logarithmic scale, respectively.

From the Nyquist plots one can see that the diameter of the semicircles decreases with methanol concentration. The points of interception of the semicircles, or their extrapolations, with the *ReZ*-axis move to the lower impedance values as the concentration of methanol vapors increases (Fig. 3). This large change can be clearly registered by EIS. In particular, the reduction of *ReZ* values is related to a decrease of electrical resistivity of the DPPE LB film, in our case the surface resistivity. Hence, the influence of methanol gas on the impedance of DPPE LB film deposited on interdigital microelectrodes studied here can be used for reliable detection and quantification of methanol vapors by means of EIS. Note that the decrease of surface resistivity is relevant to an increase of the in-plane electrical conductivity of the DPPE LB film. The LB film can be considered to have a domain structure like many slabs that are closely located at the LB film surface and have close but somewhat different dielectric properties. The electrical current rises due to the flow of free electric charges across each slab, and the capacitive current rises due to the accumulation of charges at the boundaries between the slabs [26, 27].

In Fig. 3 it is also seen that at low frequencies the large depressed semicircle is followed by a loop. The latter is due to capacitive charging of gold interdigital microelectrodes and corresponding decrease in LB film resistance at low frequencies. Actually, the loops that takes place in the two-electrode setup applied in the present study result from the change in the resistance of the LB film due to diffusion of mobile electric charges into the LB film.

Clearly, the variations in the frequency-dependent electrical impedance values due to the impact of the methanol vapors is relevant to the modification of dielectric properties of the LB film, i.e., the change in its complex dielectric permittivity. The semicircles in Nyquist plots (Fig. 3) contain information on the change of dielectric properties of the studied DPPE LB film. The spectral changes seen in Fig. 2(a,b) suggest changes of dielectric relaxations [28–31] in the LB monolayer exposed to methanol vapors. This response of the LB film is related to the modification of its dielectric properties due to adsorbed methanol gas molecules. Such modification can be correlated with the frequency f_{max} corresponding to the characteristic local maximum in each of the *ImZ*(*f*) spectra recorded for DPPE LB films in the presence of the methanol vapors (Fig. 2b). As seen from Fig. 2(b), the observed peak in *ImZ*(*f*) spectra is shifted towards the higher frequencies as the concentration of the methanol vapors increases. This frequency shift (Fig. 4) can be also used for detection and quantification of methanol vapors by EIS technique.

Additionally, the tangent loss ($tan\delta$) can also be used to characterize the change of the dielectric properties of the studied DPPE LB monolayer affected by methanol vapors. The value of $tan\delta$ can be determined from the measured impedances: $tan\delta = Im\varepsilon/Re\varepsilon = ReZ/(-ImZ)$, where ε is the complex dielectric permittivity of the studied LB layer. Note, the values of ε for the tested conditions could be very difficult to be exactly determined owing to the complicated geometry of the electrodes and the geometry of the deposited LB layer.

As a demonstration of the change in the dielectric properties of the studied DPPE LB monolayer affected by methanol vapors, Fig. 4(b) presents the calculated $tan\delta$ *vs* the frequency of the applied electric field. In contrast to the measured impedances (recall Fig. 2), the sensing effect is well pronounced in a larger frequency range, in our case 0.1 Hz < f < 1 kHz), where a straightforward increase of $tan\delta$ value with the increase of methanol gas concentration takes place (Fig. 4b). Clearly, in this way one can perform a secondary quantification of the methanol gas concentration by use of DPPE LB molecular monolayer and EIS.

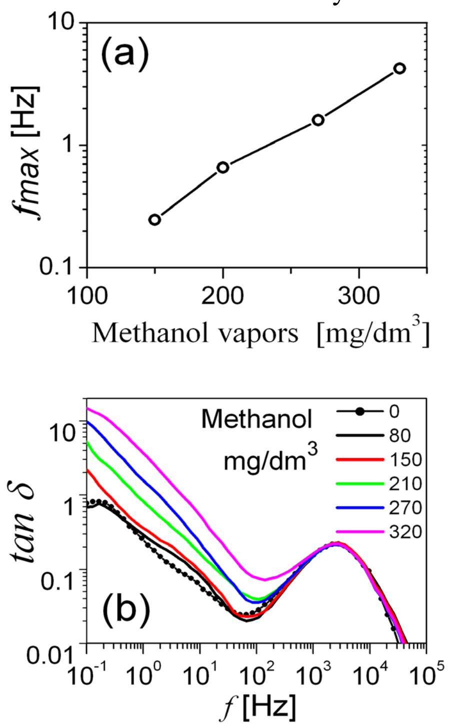

Fig. 4. (a) Frequency f_{max} determined for the studied DPPE LB film *vs* the concentration of methanol vapors;

(b) Tangent loss for DPPE LB film *vs* the frequency of the applied electric field.

The full description and physical interpretation of the modification of the electrical and dielectric properties of the DPPE LB film exposed to methanol vapors requires data obtained by modeling of the complex electrical impedance and complex dielectric spectra, as well data from complementary electrical measurements, e.g., by use of linear voltage sweeping voltammetry and cyclic voltammetry. Since the LB film morphology could affect the process of adsorption of methanol gas molecules on the film surface, the structural properties of the LB film at macro- to nano-level have to be also taken into account, hence the physical interpretation would be rather complicated. In particular, the LB film morphology will strongly affect the analysis of impedance spectra for extraction of numerical information by fitting an equivalent electrical circuit [27, 32] assembled by resistors and capacitors representing the dominant components of the studied LB film [26, 27].

CONCLUSIONS

In summary, the electrical impedimetric response of a phospholipid DPPE LB film to methanol vapors was studied at room temperature by applying electrochemical impedance spectroscopy (EIS). DPPE LB film deposited on interdigitated microelectrodes was examined at various concentrations of methanol vapors. The results show that the changes in the complex electrical impedance of DPPE LB film due to adsorption of methanol gas molecules are well detectable. In particular, the reduction of the surface resistivity of the DPPE LB film deposited on interdigitated microelectrodes can be used for detection of methanol vapors. Besides the electrical impedance characteristics of the DPPE LB film, the adsorbed methanol gas molecules lead to frequency-dependent variations in its dielectric properties. Such changes of the impedimetric response can be also used to detect methanol vapors.

The results obtained from this study are certainly promising and the methodology will be further investigated, e.g., by measurements with a four-electrode setup of EIS. Combining EIS and phospholipid LB films one can develop electrochemical biosensor micro-devices. Further, EIS measurements can provide information on the electrical and dielectric properties of phospholipid LB films in the in-plane direction, as well as on their change upon vapors of volatile organic compounds, such as methanol.

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