Multivariate Processing of Atomic-Force Microscopy Images for Detection of the Response of Plasticized Polymeric Membranes

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Received March 7, 2014

Abstract—The possibility of using the atomic-force microscopy as a method for detection of the analytical signal from plasticized polymeric sensor membranes was analyzed. The surfaces of cadmium-selective membranes based on two polymeric matrices were examined. The digital images were processed with multivariate image analysis techniques. A correlation was found between the surface profile of an ion-selective membrane and the concentration of the ion in solution.

DOI: 10.1134/S1070427214030112

The particular interest in chemical sensors as devices for analysis of liquid objects is due to the several characteristic features of devices of this kind: simple measurement procedure, weak effect on a sample under study, and fast speed of analysis. The potentiometric sensors, ion-selective electrodes (ISEs) \cite{1} and ion-selective field-effect transistors are the most widely used among sensors with electrochemical detection \cite{2}. The sensor membrane is the most important part of an ISE, its composition determines the characteristics of a sensor, such as the sensitivity, selectivity, detection limits, etc. Membranes for potentiometric sensors can be fabricated from chalcogenide glasses, single and polycrystals, and plasticized polymers. Electrodes with polymeric plasticized membranes are widely used in research activities because it is rather simple to vary the membrane composition and this enables wide variation of the analytical properties of sensors.

Extensive studies of the theory of ISE functioning have been carried out. This issue has been the object of numerous studies by both Russian and foreign researchers \cite{2–4}. The amount of knowledge about the state of the membrane surface before and after interaction with an object being analyzed is rather small despite that this information may be of use for understanding of processes at the membrane–solution interface. If available, data of this kind would expand the variety of applied problems solved with ISEs.

Modern materials science employs various devices and methods to study surfaces and related processes. For example, chalcogenide glassy membranes have been studied by X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS) \cite{5}. A combination of XPS and static time-of-flight SIMS has been used to study chalcogenide glasses modified with an organic layer \cite{6}. Despite that, strictly speaking, both methods are
destructive and require vacuum in the working chamber, they have been used to analyze plasticized poly(vinyl chloride) (PVC) membranes [7]. To assess the composition and surface structure of the plasticized membranes whose properties were described in [8], the authors combined the XPS and scanning electron microscopy (SEM).

The methods based on microscopic analyses have been long successively used to study objects of both biological and nonbiological types. The gradual improvement of the devices made it possible to pass to next orders of smallness and to study samples on the nanolevel, e.g., by atomic-force microscopy (AFM). An additional advantage of the given method consists in that it is not necessary to create a vacuum in the measuring chamber to scan a sample. This distinction makes AFM demanded in analyses of fragile biological or any other objects, including those with water on their surface. The AFM helps to solve various problems in numerous fields of science. The AFM is used to study nanocomposites [9], mechanical properties of elastomer composites [10], and surfaces of ion-exchange membranes [11] and to make a spacial analysis and assessment of morphological features of biological objects [12–16].

Topographic maps of polymeric plasticized membranes of various kinds and compositions were analyzed, e.g., for Ca\(^{2+}\)-selective membranes in [17]. The authors assessed the influence exerted by the methods used to prepare samples and by the amount of plasticizer on the structure of the membrane surface. It was shown that raising the content of the plasticizer in the membrane formulation substantially reduces the mechanical strength and surface roughness of a membrane. It was noted that the surfaces of thin films and thick membranes with identical compositions markedly differ. The surface of a thick membrane is in a nearly liquid aggregative state, but this does not preclude obtaining a high-quality AFM image.

In [18], Cr(VI)-sensitive polysiloxane membranes containing TOPO (trioctylphosphine oxide) and TBP (tributyl phosphate) as ionophores were examined. The authors describe changes in the chemical composition and physical changes in the surfaces of both types of membranes on their being brought in contact with a K\(_2\)Cr\(_2\)O\(_7\) solution. Analyzing the AFM images they obtained, the authors state that the surface of a TOPO-containing membrane fully changes upon the contact with a millimolar solution of potassium bichromate for 1 h. The images show nodes whose formation is attributed to the interaction of the ionophore and Cr\(_2\)O\(_7^{2-}\) ions. The surface of TBP-containing membranes also changes.

Later it was shown in a study by AFM that soaking of plasticized membranes sensitive to Pb\(\text{II}\) cations in a lead nitrate solution with a concentration of 1.0 × 10\(^{-3}\) M for 24 h substantially changes the roughness parameters of their surface as compared with a membrane soaked in distilled water. The authors attributed this difference in morphology to the coordination of Pb(II) and ionophore on the surface. Nevertheless, the studies concerned with the surface of ion-selective membranes have made no attempts to find a correlation between changes in the surface topography of a membrane and the concentration of ions in the solution contacting with this membrane.

In the present study, we examined by means of AFM the surface of plasticized polymeric membranes. The membranes had similar sensitivities to Cd\(^{2+}\) cations and contained \(N,N'\)-diethyl-\(N,N'\)-ditolyl-diamide of dipicolinic acid (EtTDPA) as ionophore.

The goal of our study was to find a correlation between changes in the surface profile of membranes and the concentration of a solution with which they were brought in contact. This information may be of use for describing processes that occur at the membrane–solution interface. If, in addition, the surface morphology of a membrane varies in characteristic manner with the solution concentration, the AFM can be used as a method for detecting the analytical signal from a sensor. In a system of this kind, the volume of a sample being analyzed may constitute several microliters, which is of huge practical interest.

**EXPERIMENTAL**

In this study, we examined sensors sensitive to cadmium ions, with membranes based on \(N,N'\)-diethyl-\(N,N'\)-ditolyl-diamide of dipicolinic acid, suggested in [20]. The main parameter of a potentiometric sensor is the sensitivity studied by the calibration method against a set of standard solution of an individual ion in the concentration range 10\(^{-7}\) × 10\(^{-3}\) M. The sensitivity of a sensor is determined by the slope of the linear part of the electrode function. The slope is calculated by the least-squares method and its theoretical value for doubly charged ions is 29.6 mV dec\(^{-1}\) under the standard conditions. The sensors under study, with a PVC matrix, demonstrated the slopes of 25.8 mV dec\(^{-1}\). Sensors with a similar membrane composition, but based on a silicone matrix, were studied additionally and their slopes were found to be 26.5 mV dec\(^{-1}\). Because potentiometric sensors with two membranes based on different polymeric