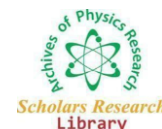




Extended Abstract

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Electrical potential near hydrated solid surface by pH spin probes and labels

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Statement of the Problem: Many solid-phase materials, for instance, porous and nano structural objects as well as the systems of specific functionality are widely used in aqueous solutions as promising heterogeneous catalysts of various reactions, can serve as suitable carriers for catalytically active organic and bioorganic groups and enzymes, and also be adsorbents of large and small molecules. The properties of solid-phase materials are affected therefore, both the chemical nature of the solution and some specific conditions are arising in the phase and on the surface of these materials. Surface electrical potential (SEP) is among the most important surface characteristics of these materials. At present, there is no method for measuring SEP of hydrated porous and nanostructured materials. Some of the most important parameters of mesoporous materials are Stern potential of double electrical layer (DEL) and surface charge because of the pivotal role they play in the adsorption of charged molecular species. There are not any conventional and easy-to-perform techniques used to measure Stern potential in porous systems. The purpose of this work is to measure Stern potential in a specific case, i.e., practically cylindrical nanosized hydrated channels of the mesoporous molecular sieves (MMS) MCM-41 and SBA-15 with channel diameters ranging from 2.3 to 8.1 nm using pH-sensitive nitroxide radicals (NR). A technique for direct measurement of the near-surface (Stern) potential using pH-sensitive NR was developed. Negative and positive values of Stern potential for the positively and negatively charged surface of MMS channels were found. The ranges of pH of external solution for the near-zero charge, boost-charging of the channel surface and for dissociation of functional groups in the MMS studied were found. Many biophysical processes such as insertion of proteins into membranes and membrane fusion are governed by bilayer electrostatic potential. At the time of this writing, the arsenal of biophysical methods for such measurements is limited to a few techniques. Here we describe a, to our knowledge, new spin-probe electron paramagnetic resonance (EPR) approach for assessing the electrostatic surface potential of lipid bilayers that is based on a recently synthesized EPR probe (IMTSL-PTE) containing a reversibly ionizable nitroxide tag attached to the lipids' polar headgroup. EPR spectra of the probe directly report on its ionization state and, therefore, on electrostatic potential through changes in nitroxide magnetic parameters and the degree of rotational averaging. Further, the lipid nature of the probe provides its full integration into lipid bilayers. Tethering the nitroxide moiety directly to the lipid polar headgroup defines the location of the measured potential with respect to the lipid bilayer interface. Electrostatic surface potentials measured by EPR of IMTSL-PTE show a remarkable (within $\pm 2\%$) agreement with the Gouy-Chapman theory for anionic DMPG bilayers in fluid (48°C) phase at low electrolyte concentration (50 mM) and in gel (17°C) phase at 150-mM electrolyte concentration. This agreement begins to diminish for DMPG vesicles in gel phase (17°C) upon varying electrolyte concentration and fluid phase bilayers formed from DMPG/DMPC and POPG/POPC mixtures. Possible reasons for such deviations, as well as the proper choice of an electrostatically neutral reference interface, have been discussed. Described EPR method is expected to be fully applicable to more-complex models of cellular membranes.

Aim: The aim of this study is to develop the method for measuring SEP of different solid phase hydrated materials by EPR of pH sensitive nitroxides (NR) as spin probes and labels.

Methodology & Theoretical Orientation: A variety of nitroxides with the range of pH-sensitivity from 2 to 8.5 pH were incorporated into nanoporous and nanostructured inorganic oxides as powders and membranes and a diversity of organoinorganic hybrid materials both by adsorption from aqueous solution and through covalent binding technique. pH-dependent parameters of EPR spectra were measured through monitoring pH in a bulk solution and inside materials. Anionic phospholipids play many roles in biophysical processes.

Findings: The negative and positive values of stern potential for the positively and negatively charged surfaces were measured from the characteristic shifts of the EPR titration curves for the slow-motion NR located in the material near-surface about those for a bulk solution. Stern layer thickness for mesoporous silicas was determined from the near-surface electrical potential profile using a model of practically cylindrical nano sized hydrated channels of the mesoporous silicas with channel diameters ranging from 2.3 to 8.1 nm. **Conclusion & Significance:** A unique technique for measuring the near-surface (Stern) potential as well as Stern layer thickness and surface charge based on EPR of pH-sensitive nitroxides as spin probes and labels have been developed for a wide range of hydrated porous and nanostructured materials with a great potential for adsorption processes and heterogeneous catalysis.

Bottom Note: This work is partly presented at 4th International Conference on Physical and Theoretical Chemistry September 18-19, 2017, Dublin, Ireland