The behavior of refractive index for water and aqueous solutions close to the Nafion interface

N.F. Bunkin[1],

A.M.Prokhorov General Physics Institute, Russian Academy of Sciences, Vavilova st., 38,

119991, Moscow, Russia

Here we describe our experiments on the modulation interference microscopy devoted to the study of the spatial distribution of refractive index n of water and some aqueous solutions close to the Nafion interface in the optical frequency range. As was obtained in these experiments, at the Nafion interface the value of n for pure water exceeds by a factor of 1.1 its equilibrium value; at moving away from the interface the refractive index falls, taking on its equilibrium value in the bulk of water at the distance of $R \approx 50$ µm from the interface. The value of R will be hereinafter termed as the effective radius of the Nafion influence upon the refractive index of a liquid; this characteristic was of the main interest in our experiments. The same way we investigated the effect of Nafion in the water-free Glycerol and the water – Glycerol mixtures at various content of water. It occurred that the Nafion does not affect the water-free Glycerol, while in case of the water – Glycerol mixtures the value of n at the interface is less than that in the bulk of the liquid. The refractive index of the mixture grows at moving away from the interface, acquiring its equilibrium value at some distance R from the interface; now the magnitude of R increases at growing the content of water, asymptotically approaching to the value of $R \approx 50$ µm, relevant for pure water. As the refractive index for Glycerol is higher than that for water, it is possible to assume that the area adjacent to the Nafion interface becomes enriched with the molecules of water, i.e. Nafion exerts a selective influence upon these molecules. We also measured the spatial distributions of the value of n for various aqueous solutions of electrolytes. It appeared that due to the presence of Nafion some ions exhibit the specific effect on the refractive index of the liquid. Indeed, as the Nafion membrane has the ion-exchange properties, it can adsorb the certain type of ions (for the sake of definiteness, let us consider that these are cations), whereas anions are not exposed to the Nafion membrane. This gives rise to change of the pH value of the solution. For example, in case of aqueous NaCl solution the Nafion membrane adsorbs the sodium ions, which results in generation of hydrochloric acid in the liquid. For different concentration of the solution the time dependences of pH were measured immediately after immersing the Nafion plate in the liquid sample; these dependences are of non-monotonic character. The changes in pH value are of irreversible character; after removal of the Nafion plate from the liquid sample the latter still exhibits the acidic properties. At the same time, for aqueous solutions of salts of some polyvalent metals the

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[1] E-mail: nbunkin@kapella.gpi.ru

value of pH does not change at presence of Nafion; that has allowed us to measure correctly the dependence of R versus the concentration of such salts. It occurred that the value of R decreases with growing the content of ions, approaching zero at the ionic concentration of $C = 10^{-1}$ M. The run of the function $R(C)$ allows us to assert that the effect of decreasing R cannot be due to the Coulomb screening of electrostatic field, which, probably, arises at the Nafion interface in the process of swelling in water. Finally, the temperature dependence of R was measured: for a wide enough range of temperatures the value of R grows almost linearly with temperature. These experimental data can be interpreted in terms of the cluster model for the molecules of water, see, for example, [1]. Such clusters can be formed close to a hydrophilic surface (the surface of Nafion in water is related to this type) and are caused by presence of hydrogen bonds. Such clusters can possess by much higher electronic polarizability with respect to separate water molecules that explains the growth of the refractive index in the optical frequency range. Indeed, the refractive index n in the optical frequency range is expressed by the known Lorenz – Lortentz formula $\dfrac{n^2-1}{n^2+2} = \dfrac{1}{3}\alpha_e N$, where α_e is the electronic polarizability, and N is the bulk density of molecules. As the water is practically incompressible, the value of N would hardly exceed its equilibrium magnitude close to the Nafion interface, so the growth of α_e is the only reasonable mechanism of increasing the refractive index. Additionally, the presence of such molecular clusters means that the interactions between molecules are of a collective character, which basically elucidates the presence of the long-range order in the behavior of refractive index both in the pure water, and in the Glycerol - water mixture. At last, these clusters should be destroyed by ions – the centers of spherically symmetric electrostatic field, which explains the fact that the value of R approaches to zero in the electrolyte solutions. However within the framework of this model it is not yet possible to interpret the growth of R with temperature, as the intensive thermal motions of molecules should effectively weaken the attractive interaction between such molecules in the cluster.

1. R. Roy, W.A. Tiller, I. Bell, M. R. Hoover, *The Structure Of Liquid Water; Novel Insights From Materials Research; Potential Relevance To Homeopathy*, Journal of Materials Research Innovations, **9**, No. 4, 577 – 608 (2005).