Nile red lipophilic anions interactions at organic aqueous interface - a way to visualize water and ion transport in ion selective membranes

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Nile red dye exhibits peculiar optical properties at organic-aqueous interfaces [3,4]. In such environments, its emission is changing due to protonation especially if formed cations can be stabilized by lipophilic anions present in either phase. This is observed as decrease of the emission intensity at ca 620 nm and formation of another emission maximum at ca 675 nm, visually this is observed as a change of the color of sample from red to blue.

These effects have been reported for interfaces of aqueous and organic media, especially in the presence of acids and surfactants in aqueous phase. However, interface of organic liquid (plasticizers) and aqueous phase is also formed within the receptor layers in sensors, especially in ion-selective membranes containing plasticized PVC, together with ion-exchangers and ionophores. In case of cation selective sensors typically used ion-exchanger are: sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate or potassium tetrakis(4-chlorophenyl)borate, i.e. lipophilic anions are present in the system. Adding Nile red to classical composition of the receptor is not affecting analytical performance (selectivity, sensitivity, linear response range), however, it offers a unique opportunity to observe gradual hydration of the receptor, in course of necessary pre-treatment.

Gradual partition of aqueous phase into receptor results in formation of protonated Nile red (where aqueous phase in the presence of excess of organic one – plasticizer is a source of H^+ ions). Formed cations are stabilized with ion-exchanger anions, resulting in a change of the membrane colour from red to blue. Thus, the process can be easily visually or fluorimetrically monitored.

Interestingly, for fully hydrated membrane upon contact with ions to which the membrane is selective, due to their preferential binding by neutral ionophore present in the receptor layer, hydrogen ions are expelled from the receptor (ion-exchanger anions are compensating ionophore – primary cations charges) resulting in deprotonation of Nile red. This can be observed visually or in emission mode as change of the colour of the membrane from blue to red or strong increase of emission at ca 620 nm.

Thus, introduction of Nile red dye to the ion-selective membrane composition enables colorimetric/ fluorimetric insight into process of ion-selective membrane preparation for sensing.

Keywords:
Nile red, ion selective membranes, ion transport, water transport, interfacial phenomena

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