Studies of Arenediazonium Ions Behavior in the Complex Matrix

Jolanta Narkiewicz-Michalek[1*], Andrzej Sienkiewicz[1], Marta Szymula[1], Carlos Bravo-Diaz[2]

[1] *Maria Curie-Sklodowska University, Faculty of Chemistry, 20-031 Lublin, Poland*
[2] *Departmento de Química-Física, Universidad de Vigo, 36-200 Vigo, Spain*

**jolanta.narkiewicz-michalek@umcs.lublin.pl*

One of the important limiting factors in the application of ArN_2^+ ions for quantitative investigations of the structure and composition of association colloids and emulsions is their stability. In our presentation the spectroscopic and electrochemical studies of dediazoniation reaction in aqueous solutions containing surfactants and/or other additives (i.e. phenolic antioxidant) are presented for para substituted arenediazonium salts. The aim of the studies was to figure out the effect of different factors on the kinetics of ArN_2^+ decomposition. By fitting best the integrated first-order kinetic equation to the experimental data (absorbance of ArN_2^+ at the appropriate wavelength vs. time), the dediazoniation reaction rate constants k_{obs} were calculated at different temperatures. Then from the Arrhenius plots activation energies and entropies were found. It has been proved that stability of arenediazonium ions depends to a great extent on the character of substituent, e.g. CH_3- and Br-groups show a retarding effect on the dediazoniation reaction. The addition of the increasing amounts of surfactant to the system causes the increase of the reaction rate up to the CMC. Above the CMC, the abrupt drop of rate constant to the values somewhat higher (for CTAB and TX-100) or slightly lower (in the case of SDS) than in the buffered aqueous solution was observed. It means that the SDS micelles stabilize ArN_2^+ ions but the effect is rather poor and depends on the substituent type. Nonionic and cationic surfactants exhibit an opposite effect.

The same systems were investigated by means of the differential pulse voltammetry (DPV) method. The peak potential, E_p, and the peak current, I_p, of ArN_2^+ were measured in the solutions of TX-100, CTAB and SDS. All measurements were carried out at pH = 1.81 and T = 25°C. From the obtained results it can be concluded that the most pronounced changes of the peak potential and peak current are observed at the surfactant concentrations below the CMC. At higher surfactant concentrations these parameters remain approximately constant. The addition of propyl gallate to the p-NOBD solution results in the decrease of reduction current, I_p, which is an evidence of the reaction proceeding between these two reagents.