Nanochemistry and Nanobiotechnology

Development of conductometric sensor for ammonium with calix[4]arene-18-crown-6 tetrasulfide as a receptor probe

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Ammonium sensing is of great analytical importance for a variety of environmental and medical concerns and in wide range of ammonium-related quantitative techniques for other compounds. Aiming at developing a highly selective, sensitive and reproducible method for ammonium determination in solutions, we turned to the properties of the calixarene materials, which appeared to be key asset in the selective recognition of both the charged species and the neutral molecules, as shown from the existing reports.

For the sensor development, calix[4]arene-18-crown-6 tetrasulfide was synthesized and immobilized on the surface of the gold interdigitated electrodes. Existence of the terminal sulfide groups in the nanomaterial structure allowed directing the receptor molecules to the planar gold surface by a self-assembly principle. Injection of ammonium to the measuring cell both in a single-channel and differential measuring modes showed the sensors' sensitivity to ammonium in a linear concentration range of 0.01–1.5 mM. The selectivity coefficients of the calix[4]arene-based sensors in the aqueous solutions of the sodium, potassium, magnesium, calcium and aluminium ions were the following: 3.8×10^{-1}, 2.8×10^{-1}, 9.8×10^{-2}, 1.2×10^{-1}, and 7.3×10^{-2} respectively, showing that calix[4]arene-based pair had high selectivity towards NH_4^+ relative to ions, known to be typical and essential components of the water samples. The coefficient of variation of the sensor' signal in the continuous measurements during a day was about 2.39%. During a period of 115 days, no considerable changes in the sensor sensitivity were observed. Other sensor's characteristics relevant for the quantitative analysis of ammonium were found to be: the dynamic concentration range 0.01–6.4 mM, the limit of detection 1.0×10^{-5} M, and the response time 5–10 s.

Acknowledgement. This work was financially supported by National Academy of Sciences of Ukraine.