SYNTHETIC RECEPTORS FOR AMINO ACIDS IN ELECTROCHEMICAL SENSORS

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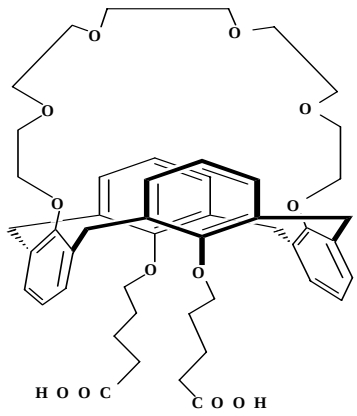
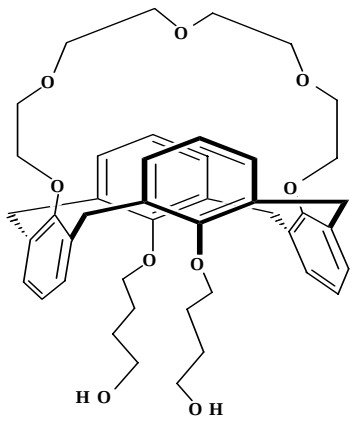
Electrochemical sensors form the largest group of chemical sensors [E. Bakker and M. T. Diaz, Anal. Chem., 74 (2002) 2781-2800] but there are very few electrochemical sensors for amino acids. The chemically modified electrodes based on electrocatalysis are applicable only for the easily oxidized amino acids like cysteine, tryptophan and tyrosine [S. Fei, J. Chen, S. Yao, G. Deng, D. He and Y. Kuang, Anal. Biochem., 339 (2005) 29–35]; and a few enzyme based electrodes [A. Curulli, S. Kelly, C. O'Sullivan, G. G. Guilbault, G. Palleschi, Biosensors & Bioelectronics, 13 (1998) 1245–125]. We report, for the first time, the possibility of using calix-crown molecules as receptors for amino acids like histidine, proline, etc, in capacitive sensors. Both calixarenes, as well as crown ethers are known to form complexes with organic amines in solutions [G. W. Gokel, W. M. Leevy and M. E. Weber, Chem. Rev., 104 (2004) 2723-2750; W. Abraham, J. Inclusion Phenomena and Macrocyclic Chem., 43 (2002) 159–174]. The calix-crown molecules used in the present work bear side chains ending in either hydroxy group or carboxylic groups which enable anchoring on Si / SiO_2 / Si_3N_4 or the so-called EIS (electrolyte – insulator – semiconductor) structures. The capacitance measurements were done at 10 kHz frequency over the range of – 100 to + 2800 mV vs. SCE. The shift in the flat band potentials with the addition of amino acids was indicative of the complexation phenomena and can be used quantitatively. The admittance spectra over the frequency range of 100 kHz to 10 mHz at 2700 mV showed a gradual decrease in admittance with increasing concentration of amino acid. The experiments were done in 0.05 M H_2SO_4 medium where the amino acids exist in protonated forms. They form complexes through insertion of protonated amino groups into the cavity formed between the calixarene and crown ether moieties.



1,3-(Diethyl-5-oxavaleric Acid)-calix[4]arene-crown-6



1,3-(Di-4-oxabutanol)-calix[4]arene-crown-5