The Mechanism of Electrode Reaction in Carbamide and Carbamide-Chloride Melts. Modeling and Experimental

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Electrode reactions in molten carbamide have been studied by experimental methods: cyclic voltammetry in combination with IR spectroscopy, NMR and chromatography. Due the fact that we were unable to identify a number of electrolysis products in the gas phase and melt, the mechanism of electrode processes based on experimental data could only be of approximate character.

A large amount of ammonia and a small amount of CO and CO_2 have been found in the cathode gases of carbamide melt by means of IR spectroscopy and gas cromatography. An intense CO_2 band is also present in IR spectra of anode gases; in addition, traces of CO and a number of unindetifided bands in the range 1500-1700 sm^{-1} have been found. The presence of N_2 in them has been shown using chromatographic analyses. The IR spectra of the catholyte and anolyte are identical and have a signal from the carbonyl ion of carbamide, ammonium ion and a signal characterizing the C-N bond. Accumulation of NH_4^+ ions in the melt was shown by means of NMR. On the basis of the results obtained by us the scheme of electrode reaction can be proposed:

$$2CO(NH_2)_2 \xrightarrow{+2e} 2NH_3 + CO + O^{2-} + NH_2CN \quad (1)$$

$$2CO(NH_2)_2 \xrightarrow{-6e} CO_2 + N_2 + 6H^+ + NH_2CN \quad (2)$$

Then the overall reaction is:

$$8CO(NH_2)_2 \rightarrow 3NH_3 + 3CO + CO_2 + N_2 + 3NH_4OH + 4NH_2CN \quad (3)$$

It is assumed that electrolysis product may be cyanamide as the simplest substance in terms of IR spectroscopic data for the melt.

When performing the quantum-chemical simulation of the electrode process in molten carbamide, it was assumed that the initial electrolysis stage would be the formation of cation and anion radicals. It has been shoun by calculating the total spin density that the most probable site of bond rupture in anion radical is the C=N bond and in cation radical the C=O bond, and the mechanism of electrochemical transformations in molten carbamide has been proposed:

$$5H_2NCONH_2 \xrightarrow{+e} CO + 2[NH_2]^- + H_2O + 2H_2N\text{-}CO\text{-}NH\text{-}C(NH_2)=NH \quad (4)$$

$$3H_2NCONH_2 \xrightarrow{-e} N_2 + CO_2 + 6H^+ + H_2N\text{-}CO\text{-}NH\text{-}C(NH_2)=NH \quad (5)$$

Then the overall reaction is:

$$8H_2NCONH_2 \rightarrow N_2 + CO_2 + 3CO + 6NH_3 + H_2O + 2H_2N\text{-}CO\text{-}NH\text{-}C(NH_2)=NH \quad (6)$$

Comparison of the electrolysis products obtained on the basis of experimental investigations and theoretical calculations shows a difference only in the determination of the reaction product that is in the liquid phase.

As was pointed out, cyanamide was called roughly the simplest compound, in whose molecule there are C=N and N=H bonds (according to IR-spectroscopic data of the melt). However, the formation of biuret is quite probable according to Eqs. (4-6) since its structure also corresponds to the spectroscopic data; besides, biuret is one of the main products of thermal carbamide decomposition.