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Thematic course: Synthesis, structure, properties and agrochemical use of new potentially biologically active derivatives of triethanolamine. Part I.

Tris(2-hydroxyethyl)ammonium salt synthesis in aliphatic dicarboxylic acids

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Abstract

Tris(2-hydroxyethyl)ammonium salts of aliphatic C2-C9 dicarboxylic acids were synthesized and characterized. The acid properties impact assessment on stability and physical properties of synthesized salts was shown. According to potentiometric titration curve analysis there were defined principles of selective formation of salts with different cation-anion ratios (1:1 or 1:2), which are consequences of electrostatic impact relied on a difference of carboxylic groups dissociation constants (ΔpKa).

Recently applied criterion for crystalline structure prediction in tris(2-hydroxyethyl)ammonium salts (symmetrical and asymmetrical carboxyl anion oscillation frequency difference in Fourier-IR spectra) was shown to be insufficient without special structure issue acknowledgments.

Structure commonality of acid and normal protatrane and quasiprotatrane derivatives was defined. Thus, the acid protatranic salts transform anion configuration into stable *gauche*-conformation in contradistinction to normal protatranic and quasiprotatranic ones owing to structure stabilization intentions in solid state. The cation hydroxyethyl fragments of normal protatranic salts form hydrogen bonding only with two anions (whereas the other salt types with three ones), which provides significant changes in cation structure symmetry. Protatrane quasicycle disruption and transformation into quasiprotatrane conformation allow hydrogen bonding with N-H ammonium proton, so this bonding in aliphatic dicarboxylic acid quasiprotatranes takes place solely with hydroxyethyl fragment oxygen atom deflected from standard protatrane plane. All cation C-C bond lengths differ from standard sp^3 C-C length 1.54 Å and equal 1.49-1.51 Å, so that vicinal C-O and C-N bonds exist exceptionally in *gauche*-conformation, which also demonstrates the field-effect domination in organic chemistry.

Functional group insertion (e.g. hydroxyl, methylene, ketone) in anion resulted in melting point decrease and transition into amorphous or liquid phases compared to corresponding unsubstantiated acid anion derivatives.

The resulting tris(2-hydroxyethyl)ammonium salts of aliphatic dicarboxylic acids principally appertain to ionic liquid class and hence that can be utilized in some specific ways related to these compounds.

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