THERMODYNAMIC PROPERTIES OF SUBSURFACE MONOLAYERS AND STRUCTURAL ASSIGNMENTS OF BULKY AGGREGATES BASED ON DICATIONICS

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Dicationic onium salts (DOS) with long alkyl substituents ("tails") perform excellently as surface tension reducers for the air/water and oil/water interfaces emerging as effective agents for surfactant-enhanced petrol recovery [1] from both nature basins and industrial reservoirs. Many other possible applications were supposed on a basis of unique properties of DOS as ionic liquids, ionic plastic crystals, and non-volatile electrolytes. For a task-oriented usage, detailed knowledge of thermodynamics in the fields looks needed. Small libraries of DOS encompassing majority of typical heads, spacers and counter-ions were constructed [2], their thermal, surface-reducing, and other properties were studied and compared with available literature data. Molecular structures of all library items were thoroughly inspected, and all usual experimental procedures for structure elucidation were maintained. Molecular geometry and electronic structure of virtual dications were evaluated with *ab initio* calculations, some representative examples were interpreted in a frame of Bader quantum theory of atoms in molecules QTAIM, reduced density gradient RDG and independent gradient model IGM approaches. Dicationic imidazolium halides DIH with short spacers dissociate into free ions (behave as strong electrolytes) in diluted water solutions. With a concentration rising, DIH molecules combine into supermolecular aggregates in bulky volume, and, in parallel, migrate to solution/air interface, slowly and far from diffusion control. Surface tension and dilatational rheology measurements made simultaneously and independently by DuNouy ring and hanging drop dynamical methods identified highly resilient layers of DIH on the interface, with extremely large dilatational moduli. Concentration dependences of storage and loss moduli in combination with tension dependences reveal lucid signs of an organized adsorbed layers at a first stage and further disordering. Highly negative Gibbs energies ΔG of interface layers formation support this notion. Specific for DIH models of supramolecular organization in volume and at the interfaces have been proposed, their differences from generally accepted Gemini style micellization analyzed from structural and thermodynamic point of view.

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