# Physicochemical bases of membrane-assisted gas absorption (MAGA) technique for carbon dioxide removal from methane-containing gas mixtures

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**Relevance of the research.** Natural gas is a significant part of the world's energy supply. This is one of the purest and most environmentally friendly types of fossil fuel. An acid gas removal operation is an important technological step in the route of natural gas processing. The presence of carbon dioxide and hydrogen sulfide in the natural gas stream adversely impacts the heat (calorific) value and provides a number of operational problems such as pipeline corrosion and forming of gas hydrates (if the water is present). Because of that, it is necessary to remove acid gases to meet the pipeline specifications. The conventional amine scrubbing technology using aqueous solutions of amines (monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA)) is well known and are considered as a state-of-the-art technology. Nevertheless, that technique is characterized by high capital and operating costs, a large footprint, and high energy consumption. The efficiency of $CO_2$ removal process can be improved by developing new absorbents with high sorption capacity towards $CO_2$ and/or developing new and improving existing gas separation methods.

Ionic liquids (ILs) are an attractive class of substances for acid gas absorption, since they have unique properties: low saturated vapor pressure, thermal stability, and high acid gases sorption capacity. It is possible to finely tune ILs physical and chemical properties by variating cations and anions or introducing the functional groups into structure. However, most ILs with a high $CO_2$ sorption capacitates contain fluorine-containing anions, which tend to hydrolyze. In this regard, for the efficient removal of acid gases, the main attention should be paid to the design of new environmentally friendly ionic liquids. Therefore, from the point of view of creating new sorbents for capturing acid gases, the synthesis of new green compounds that do not contain fluorine atoms is of great importance. From the point of view of creating new absorption materials, it is promising to develop solutions based on alkanolamines with new green ionic liquids.

Along with the development of new materials, new approaches that allows forego of energy-intensive amine scrubbing method are of great interest. Since the membrane-based process provides separation without phase transition, does not require heat supply or removal, and membrane apparatuses are characterized by the simplicity of hardware design, small footprint, and energy efficiency, they seem to be an attractive alternative to conventional chemical absorption.

A unique hybrid technique – membrane-assisted gas absorption (MAGA) provides separation without phase transitions in a single-volume mass transfer apparatus and does not require heat supply or removal. The appliance of liquid absorbents in this process increases the selectivity, while the gas separation membrane ensures the regeneration of the absorbent in a continuous steady-state mode.

**The general goal of this work** is to increase the efficiency of acid gases impurities removal process by creating new sorption materials based on an alkanolamine-ionic compound solution in water and using them as absorbents in a hybrid separation process – membrane-assisted gas absorption.

**Tasks:**

1. Synthesis of ILs with fluorine-free anions, identification of their structure and determination of their sorption properties towards $CO_2$.
2. Obtaining of MDEA-based absorption solutions containing synthesised ILs and water in different ratios as components. Selection of the most promising solution composition.
3. Experimental determination of sorption properties of the obtained solutions to $CO_2$.
4. Experimental determination of selectivity of the obtained solutions for the components of a model gas mixture based on $CH_4$ and containing admixtures of $CO_2$ and $H_2S$. Determination of the most advantageous composition of the absorption solution.
5. Determination of $CO_2$ and $H_2S$ removal process efficiency by membrane-absorption gas separation using 3 and 8 component gas mixtures as examples.

**The scientific novelty of the study** lies in the first synthesised ionic compounds, the preparation of absorption solutions based on MDEA and synthesised ILs. The selectivities of the solutions obtained this way on the components of the $CH_4/CO_2/H_2S$ gas mixture were also determined for the first time. On the experimental data the most efficient composition of the system is also determined. A new configuration of the MAGA module with hollow fibres is also proposed. For the proposed configuration, the efficiencies of the MAGA process using new absorbents are also first time experimentally evaluated using three and eight-component gas mixtures close to natural gas as examples. As a result, the proposed module efficiency is demonstrated in the problem of acid gas removal.

**Theoretical and practical significance of the work.**

The fundamental significance of the integrated approach lies in the creation and study of new absorption solutions from the point of view of studying their physicochemical properties. Applied

significance is justified by the optimisation of natural gas treatment process by membrane-absorption gas separation method. The results of the work can be useful for optimisation of the traditional method of natural gas sweetening - amine purification due to creation of new acid gases absorbents, as well as due to introduction of additional membrane-absorption gas separation module into technological schemes.

**The main provisions for the defense:**

1. Synthesis of ionic liquids based on quaternary ammonium cation with taurate and glycinate anions and their characterisation by NMR and IR spectroscopy.
2. Experimental study of the sorption capacity of aqueous solutions of MDEA with different contents of [BHEDMA][Tau] and [BHEDMA][Gly] ILs towards $CO_2$.
3. Experimental study of the sorption capacity of aqueous solutions of MDEA containing synthesised [BHEDMA][Tau] and [BHEDMA][Gly] ILs by components of the gas mixture ($CH_4$ / $CO_2$ / $H_2S$).
4. Experimental evaluation of the efficiency of the membrane-absorption method of gas separation using an aqueous solution of MDEA containing [BHEDMA][Gly].
5. Application of a new membrane-absorption gas separation hollow-fibre module in the process of acid gas removal from methane-containing gas mixtures.