Polymeric ionic liquids and their natural analogues in the synthesis of membrane materials for diffusion-driven processes

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Relevance of the research.

Organic ionic compounds - ionic liquids and their polymer analogues - have been intensively studied in recent years as a basis for the development of membrane materials for the separation of acid gases from gas mixtures and polar components of liquid mixtures during pervaporation.

Polymeric ionic liquids (PILs) are subclass of polyelectrolytes, having ionic liquid (ILs) as elementary unit, which combine the properties of low-molecular organic ionic compounds with the polymeric nature of the substance. Some unique properties of ILs, such as the ability to selectively interact with carbon dioxide (CO_2) and reversibly bind it, are also inherent in PILs. At the same time, PILs can be processed with traditional methods of polymer chemistry and formed into various functional materials. The ability to create materials of various morphologies based on compounds that are in an ionized state, regardless of the presence of a solvent, significantly expands the horizons of ILs application. For example, ILs, which have limited use in membrane technologies for the separation of acid gases due to the instability of supported ionic liquid membranes at high pressures, can be successfully used in polymerized form or in the form of an ionic gel in combination with a high-molecular-weight polyelectrolyte. However, PILs are also characterized by a number of disadvantages associated with their synthetic origin. Firstly, the production from a non-renewable source of raw materials, and secondly, the difficulty of safe disposal.

An alternative to PILs are natural polyelectrolytes. Chitosan acetate, formed by dissolving of chitosan in a solution of acetic acid, is an analogue of synthetic PILs containing an ammonium cation in the elementary unit. In addition, the high thermal stability of chitosan, as well as the ability for film formation and biodegradation, makes it the most attractive renewable raw material for the synthesis of membrane materials with properties similar to, and even superior to, synthetic PILs.

The general goal of this work is to synthase a number of polymer ionic liquids and their analogues based on chitosan copolymers with vinyl monomers and to establish a relationship between the composition and structure of the polyelectrolytes with operational and transport properties of membrane materials based on them in diffusion processes - gas separation and pervaporation

Tasks:

1. Synthesis of a number of PILs of various composition using the method of post-polymerization modification of polyvinylbenzyl chloride
2. Synthesis of chitosan copolymers with vinyl monomers of various composition and structures
3. Study of the physicochemical properties of synthesized polyelectrolytes
4. Preparation of polymer membranes of various morphologies based on synthesized PILs, chitosan copolymers and ionic liquids
5. Study of the morphology, operational and transport characteristics of membrane materials based on PILs and chitosan copolymers in the process of CO_2 separation from gas mixtures and pervaporation dehydration of tetrahydrofuran

The scientific novelty

1. A method has been created for qualitative assessment of *in situ* interaction of polymer matrices with CO_2 using ATR-IR spectroscopy. It has been established that the interaction of CO_2 with PILs is of the physiosorption nature. The position of the signal of asymmetric stretching vibrations of the O=C=O bond is determined by both the nature of the polycation and the counterion.
2. For the first time, a systematic study was carried out of the influence of the composition of PIL based on polyvinylbenzyl chloride, namely the degree of functionalization and substitution of the anion, the nature of the polycation and the nature of the anion, on the physicochemical and transport properties in the process of CO_2 separation from gas mixtures.
3. The influence of the composition and structure of chitosan copolymers with vinyl monomers on the morphological, operational and transport characteristics of membrane materials based on them in the process of CO_2 separation from gas mixtures has been established. Membranes with a mixed matrix with IL with a permeability coefficient (400 Barrer) and CO_2/N_2 selectivity = 4.2 were obtained.

4. For the first time, composite membranes based on block copolymers of chitosan with vinyl monomers were obtained and characterized in the process of pervaporation drying of THF. A connection has been established between the composition of the copolymer and its transport characteristics. Membranes with a high separation factor (β = 1487) and permeation flux (0.202 kg/m^{2}h) were obtained in the process of pervaporation dehydration of an azeotropic mixture of THF with water.

Theoretical and practical significance of the work.

A method has been developed for qualitative assessment of the interaction of carbon dioxide with polymer matrices using ATR-IR spectroscopy. A connection has been established between the composition and structure of polyelectrolytes with their physicochemical, thermophysical, physical and mechanical properties and transport properties. The obtained patterns can be used for the synthesis of new functional polymer materials with specified properties based on synthetic polyelectrolytes and their natural analogues for use as highly efficient membrane materials in diffusion-driven membrane processes.

The main provisions for the defense:

1. Qualitative assessment of carbon dioxide sorption by a polymer matrix *in situ* using ATR-IR spectroscopy;
2. Preparation of polymeric materials of various morphologies based on synthesized compounds;
3. Establishment of the dependence of the physicochemical and transport properties of synthesized PILs and materials based on them on the composition of PILs;
4. Establishing the dependence of the physicochemical and transport properties of synthesized chitosan copolymers and materials based on them on the composition and structure of the copolymer.