Switchable-polarity solvents/solutes for closed-loop osmotic energy generation and catalytic reactions

Final Report

Aims of our project were

1. to investigate whether switchable polarity components may be applied for economic energy generation by pressure retarded osmosis process as well as the theoretical investigation of the mass transport. The polarity change of solute would make possible the regeneration of the liquid phases, which then makes possible their recirculation. Moreover, investigation of the solute transport through the selective membrane layer helps to find the more advantageous operation's conditions;
2. synthesis and the application of different switchable solvents that can serve as catalysts in base-catalyzed organic reactions.

The pressure retarded osmosis, as osmotic pressure driven membrane process, are researched for the so-called blue energy generation, using the switchable polarity solute. To do it, different tertiary amines/amidines were synthesized, that can be converted from a non-ionic state to an ionic salt in liquid form by an external stimulus, such as CO_2. These switchable compounds as a new class of solvents in organic reactions will facilitate isolation of products and, more importantly, makes it possible to regenerate and to recycle catalyst/solvent mixtures as well as a new class of ionic solutes that can be regenerated and then repeatedly used for energy generation. Mass transfer models have also been developed for evaluation of the experimental results, which were also completed, for comparison, using NaCl solutions. Thus, these switchable polarity components can be used a) for energy generation and b) as catalysts in base-catalyzed organic reactions.

1.1 Ionic compounds using them for osmotic energy generation in aqueous systems

The behavior of various commercially available amine (n-butyl amine, dibutylamine, triethylamine, N-ethyl-dicyclohexylamine) + water systems were investigated in the presence of CO_2. As other possible basic components, dibutyl-(2-methoxyethyl)-amine and dibutyl-(2-(2-metoxyethoxy)-ethyl)-amine were synthesized. In these cases the amine + water + CO_2 systems were found to be reversible, but the first one was not suitable for further experiments because of its relatively high volatility. The newly, synthesized precursor for the ionic liquid species (N-etyldicyclohexylamine, Dibutyl-(2-methoxyetyl)amine) and also NaCl compounds are applied for energy generation measurement by means of the pressure retarded osmosis process and the previous component for catalytic reactions, as well. (The structure of the switchable polarity ionic solute is illustrated in Fig. 1). It is expected that this precursor of higher molecular weight has enough high boiling temperature. The research works in connections to the application of the ionic liquid or NaCl for energy generation can be divided into two areas, namely:

Two types of PRO membranes (NanoH2O from firm of NanoH2O Inc.; PFO Membrane from Porifera Inc.) were used for PRO and FO (forward osmosis) measurements.

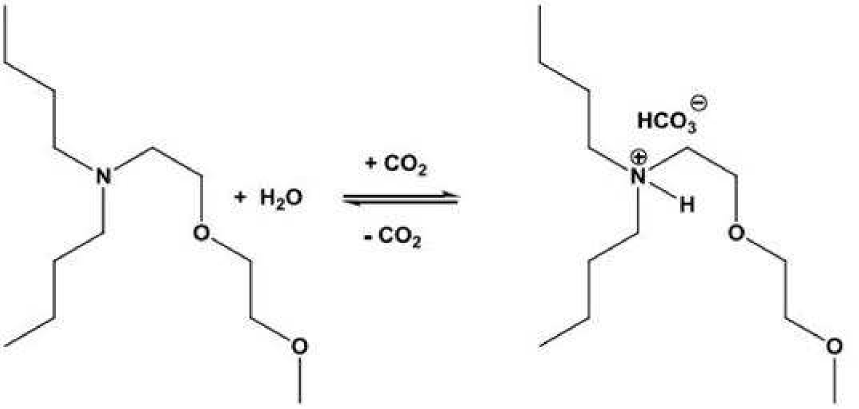

Fig.1. The structure of the dibutil-(2-2-metoxietoxi)-etil-amin as precursor and its switchable polarity ionic form

The solute concentration dependence, the effect of the hydraulic pressure difference were measured in order to improve the mathematical description of the solute and water transport according to the parallel, i.e. data obtained by PRO and FO experiments, measured data.

The usage of the ionic liquid (dibutil-(2-2-metoxietoxi)-etil-amin), by its regeneration after all cycles was carried out, during three cycles. According to the results, the regeneration of the used ionic liquid is acceptable, though the rest of the not regenerated portion of this relative expensive species is high, 1-3wt%, which have to be decreased to make this process more attractive.

As it was mentioned the main aim of this investigation to find an economic technology of closed cycle PRO process. The precipitation of the solute compound can offer such a methodology, which makes possible the removal of the solute from the thin feed solution and the diluted draw solution used for energy generation by means of a turbine. The essence of our idea is that the organic switchable component can reversibly be formed to ionic liquid by its reaction with carbon dioxide. After its usage in a PRO process, this ionic compound can be separated as organic phase, by its deconstruction at higher temperature using inert gas flow through its containing aqueous phase. According to the experiments, both the water-, and the solute fluxes increase gradually, though with lowering intensity, with the increase of the ion concentration [2]. This tendency is caused by the internal and external mass transfer resistances. This water flux data are similar to that obtained by NaCl solution at this concentration range given in mol/L.

The water permeability, A (m/sbar), coefficient and the solute permeability coefficient, B (m/s), were measured by known methods in separate experiments (not shown here). Accordingly, the known mathematical equations can power density of the process be predicted. Using these equations, the power density has been calculated under different operation conditions, focusing on the effect of the solute concentration and the high concentration draw solution. It has been stated, that the switchable polarity organic compound can economically be applied for energy generation. However, during the 1 step regeneration about 1-2% of the switchable polarity component is remaining in the feed solution, which then decreases the performance of the process. That is why, the solute remained in the feed solution should also be removed, which needs further investigation [1,2].

1.2 . **Results on the description of the solute transport during energy generation**

Mathematical description of the energy generation mass transport process and the investigation of the effect of the presence of foulant on the process efficiency is focusing on the expression of every single interface membrane concentration and on the study of the effect of the cake structural parameter. The experimental measurements were carried out using both the ionic liquid as solute and NaCl. The experiments were carried out by both pressure retarded osmosis (the high salinity solution faces the active side of membrane) and forward osmosis modes (the high salinity solution faces the support layer of membrane) [2].

The further investigation of mass transfer description through asymmetric membranes (which are generally used for pressure retarded osmosis process) has been carried out and analyzed in details, with the aim, to make more understandable of the transport behavior through s dense membrane. More papers have been published from these results in open access journals [3-8].

2. Synthesis and the application of different switchable solvents [9-11]

2.1. Formation of switchable polarity materials and investigation of their reversibility

Three types of switchable polarity solvents (reversible ionic liquids) were investigated: water containing systems (i) that can be used in osmotic energy generation, mixtures with basic organic components (ii) that can serve as catalysts in base-catalyzed organic reactions and systems containing N-heterocycles and basic organic compounds (iii) to be used in base catalyzed reactions of the N-heterocycles.

i) Amine + water systems

The behavior of various commercially available amine (n-butylamine, dibutylamine, triethylamine, N-ethyl-dicyclohexylamine) + water systems were investigated in the presence of CO_2. Complete reversibility between the ionic form (in the presence of CO_2) and molecular form (in the absence of CO_2) could be detected only in case of N-ethyl-dicyclohexylamine. The ionic liquid formed in the N-ethyl-dicyclohexylamine+water+CO_2 system could be almost completely turned back to the molecular (non water soluble) form. The concentration of the ionic liquid in water could be reduced from 0.34 mol•dm^{-3} to 1.49*10^{-3} mol•dm^{-3} based on conductivity measurements.

A two-step procedure that could be used for multigram-scale synthesis and made a further scale-up possible was also developed to produce this amine. Acetylation of dicyclohexylamine was followed by a reduction of the amide product with LiAlH4. A partial deacetylation as a side reaction was observed, so the product had to be purified by distillation.

As other possible basic components, dibutyl-(2-methoxyethyl)-amine and dibutyl-(2-(2-metoxyethoxy)-ethyl)-amine were synthesized. In these cases the amine + water + CO_2 systems were found to be reversible, but the first one was not suitable for further experiments because of its relatively high volatility. The formation of the ionic liquid in the dibutyl-(2-(2-metoxyethoxy)-ethyl)-amine +water+CO_2 system was investigated on a larger scale, using approximately 150 g of the amine. The formation of the ionic liquid was followed by conductivity measurements and was found to be complete after two hours. This system was switched back to the molecular (non water soluble) form by expelling CO_2 at 90 ^oC in 5-20 min. The time necessary for the removal of CO_2 depended on the amine/water ratio. Measurement of the amount of expelled CO_2 was used to determine the ionic liquid content of the mixture. It was found that 2% ionic liquid remained in the solution even after a prolonged heating. Concentration dependence of the conductivity of the ionic liquid, as well as solubility of the amine component in water was determined.

ii) Amine, amidine or guanidine + alcohol systems

1,4-Diazabicyclo[2.2.2]octane (DABCO) did not form an ionic liquid in the presence of simple alcohols (such as methanol, n-butanol). On the contrary, a stable, but unfortunately irreversible ionic liquid could be prepared from DABCO, ethylene glycol and CO_2.

1,8-Diazabicyclo-undec-7-ene (DBU) was found to form a salt with high melting point in the presence of even traces of water. This hindered reversibility and also practical applicability of this system.

Reaction of 2-n-butyl-1,1,3,3-tetramethylguanidine (nBu-TMG) and various alcohols (methanol, ethanol, hexanol, ethylene glycol) with CO_2 resulted in the formation of switchable polarity solvents. Reversibility could be proved by conductivity measurements.

2-t-Butyl-1,1,3,3-tetramethylguanidine (tBu-TMG) reacted with CO_2 in the presence of water, methanol or ethylene glycol to form ionic liquids. The first two systems were found to be reversible, but the last one could not be decomposed without some loss of the guanidine component. Similarly, 1,1,3,3-tetramethyl-2-i-propylguanidine (iPr-TMG) was found to form a non-reversible ionic liquid with ethylene glycol.

A detailed spectroscopic investigation (FTIR and NMR measurements) together with DFT calculations were carried out to prove the structure of ionic liquids formed from guanidine/ethylene glycol mixtures.

iii) N-Heterocycle + guanidine systems

Formation of ionic liquids in the presence of nBu-TMG, CO_2 and imidazole, pyrazole and 1,2,4-triazole was proved by NMR measurements. For efficient catalytic applications (see below) reversible systems composed of an N-heterocycle, nBu-TMG and [bmim][BF4] were also developed. The change in structure of the components in the presence and absence of CO_2 was followed by NMR investigations of cooled samples.

2.2. The application of switchable polarity solvents in organic reactions

The concept of reversible ionic liquids was planned to be used to recycle organic base catalysts in various reactions. That means, the reactions were planned to be carried out in the molecular form to use the basic component as the catalyst. Then, the formation of the ionic liquid in the presence of CO_2 might facilitate extraction of the product with an organic solvent and then the ionic liquid might be switched back to the molecular form ready to catalyze the reaction of fresh reagents. However, this methodology was found to have several pitfalls, such as good miscibility of the ionic liquid forms with several organic solvents that hinders extraction of the products, side reactions in the presence of guanidine bases, or irreversibility of catalytically active systems.

Several reactions were attempted to be carried out by this methodology, such as triazole formation via azide-alkyne cycloaddition, Baylis Hillmann reaction of benzaldehyde and 2-cyclohexen-1-one, domino reaction of 2-aminoacetophenone and benzaldehyde involving a Claisen-Schmidt condensation – aza-Michael addition, as well as Knoevenagel reaction of different substrates. Efficient catalyst recycling could be achieved in Claisen-Schmidt condensation of different steroidal derivatives and aza-Michael addition of dehydropregnenolone in the presence of N-heterocycles.

Claisen-Schmidt condensation of 5α-androstane-17-one and different aromatic and heterocyclic aldehydes as well as that of estrane derivatives (estrone and estrone methyl ether) with aromatic and heteroaromatic aldehydes was carried out using the switchable solvent (nBu-TMG +ethylene glycol). The catalyst/solvent mixture was reused three times efficiently.

17-Chloro-16-fomyl-Δ16 androstanes and estranes were synthesized in the presence of Vilsmeier-Haack reagent. Claisen-Schmidt condensation of the substrates with different carbonyl compounds was investigated using different 2-alkyl-1,1,3,3-tetramethylguanidine catalysts in alcohol solvents. The application of nBu-TMG led to the products with good to moderate yield. Recyclability of the switchable polarity solvent was also proved. In the presence of the more active tBu-TMG or iPr-TMG the reactions could be carried out under mild conditions. At the same time, the use of the latter catalysts as components of reversible ionic liquids was less favorable due to problems either in the extraction of the products or removal of CO_2.

The applicability of nBu-TMG as the catalyst in the aza-Michael addition of 3β-hydroxypregna-5,16-dien-20-one and imidazole, pyrazole and 1,2,4-triazole was investigated. The addition of an imidazolium ionic liquid to the N-heterocycle - nBu-TMG-CO_2 system made it possible to recycle both the catalyst (nBu-TMG) and the excess of the heterocycle that was necessary to push the reaction of the steroidal substrate into completion.

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