ENCAPSULATED IONIC LIQUIDS (EIL): FROM CONTINUE TO DISCRETE FLUID FOR ENHANCING TRANSPORT PHENOMENA KINETICS IN SEPARATION AND REACTION APPLICATIONS

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Introduction: Ionic liquids (ILs) are being investigated as alternative solvents in an impressive variety of separation and reaction processes [1], mainly due to their tuneable properties depending on the cation-anion selection and the advantage of their low vapour pressure.

However, a main disadvantage for ILs practical applications is the limitation in the transport properties of these solvents, which generally presents higher viscosity, density and surface tension than conventional organic solvents. In this work is presented the preparation and characterization of a new material called ionic liquid encapsulated (EIL), based on carbon submicrospheres filled of IL. This new material combines the advantages of IL and a solid support, improving the kinetics of mass transfer through the discretization of the fluid in submicrodrops, as demonstrated in its application to the absorption of ammonia [2].

Experimental: We present the new EIL material, which consists on the IL introduction into the hollow (diameter ~400 nm) of carbonaceous submicrospheres. These novel material are formed by a mesoporous shell and a core hole and were prepared from a silica precursor [3,4]. To incorporate the IL on the sphere was used a solution of acetone and IL, adding drop by drop upon the surface of the carbon, evaporating the solvent and repeating this procedure until incipient wetness. The prepared EIL systems present ~90% w/w of IL but discretizated in spherical particles with size lower than 1 μm, which drastically increases the surface contact area respect to the neat fluid.

EIL materials have been characterized by elemental analysis, adsorption-desorption isotherms of N_2 at 77 K, mercury porosimetry, thermogravimetric analysis, differential scanning calorimetry, scanning electronic microscopy, energy dispersive X-ray and transmission electron microscopy.

Tests of absorption/desorption of ammonia on these absorbent materials were carried out in a thermogravimetric analyzer and packed bed experiments. Subsequently, desorption were performed in presence of N_2 at room temperature. The experimental data were fitted to a pseudo second order [5] and Yoon and Nelson models [6] that keep us to obtain both thermodynamic and kinetic values of the absorption phenomena.

Results and discussion: In this work, EILs were prepared using a task-specific IL (1-butyl-3-methylimadazolium tetrafluoroborate, [bmim][BF_4]) with improved properties for ammonia absorption. The IL was chosen with the aid of the quantum-chemical method COSMO-RS. The IL was evaluated for the selective separation of ammonia at near ambient temperature and atmospheric pressure. EIL involves IL in the inner hollow of a carbon submicrosphere (diameter ~400 nm). EIL system allows the incorporation of 85% (w/w) of IL, getting the discretization of spherical particles with a size below 1 μm, which dramatically increases the contact area with respect to the pure fluid. We conducted a systematic characterization of the different materials. It keeps us to analyze the incorporation of IL inside the sphere. Figure 1 shows transmission microscopy images where the addition of IL seen to be in both the shell and at the core of the sphere. The different characterization techniques used allowed us to quantify and study the stability of the adsorbent material [7].

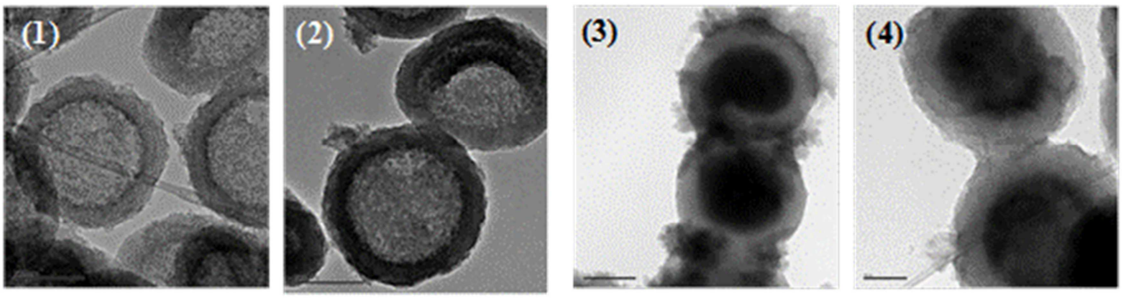

Figure 1. TEM image of empty carbonaceous submicrospheres (1, 2) and EIL system with an IL load of 80% (w/w) (3, 4).

Thermodynamic and kinetic experiments were carried out with different IL loads and using the IL solvent and carbonaceous submicrospheres in blank assays. Figure 2 shows that EIL material maintains absorption capacity of the IL but increasing the separation rate by, at least, a factor of four. Remarkably, ammonia solute is easily recovered from EIL by strippings, using the same gas flow and operation conditions than in retention experiments, being EIL materials able to be successfully used in successive absorption/desorption cycles.

Conclusions: It is reported a new type of IL-based systems which may be described as submicrodrops of IL encapsulated into carbonaceous spheres, i.e., a discretizated fluid with essentially the solvent properties of IL but with significantly enhanced transport properties, what would open new research lines in IL applications to separation and reaction processes.

The sorption experiment carried out both in gravimetric and fixed bed reactor keep us to demonstrate that the kinetic both the sorption and desorption process was higher that the observed for the IL or AC separately. So, it is proved the efficiency of the submicrosphere functionalization by using the properly IL, predicted efficiently by mean of quantum-chemical program COSMO-RS.

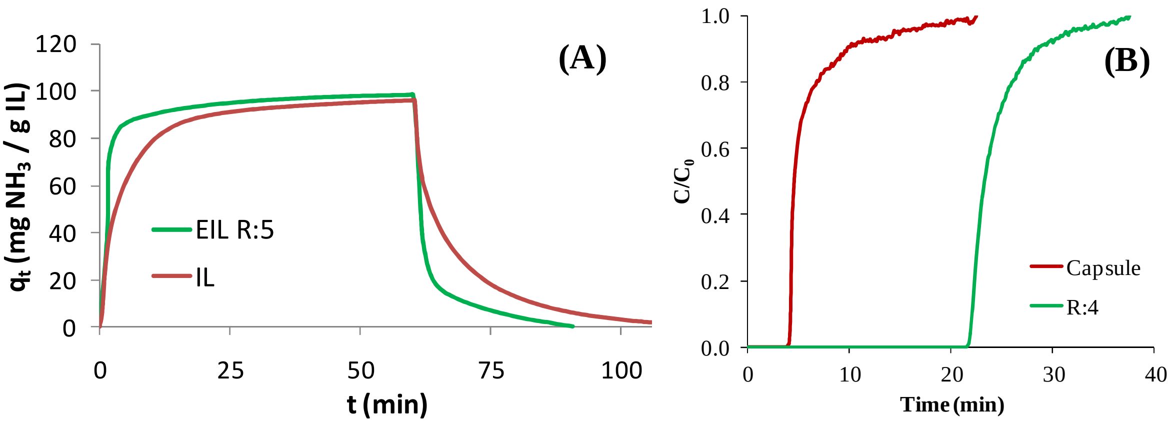

Figure 2. Thermogravimetric (A) and packed bed results (B) for IL, carbonaceous submicrospheres and EIL materials.

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