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Acetylene absorption by ionic liquids: A multiscale analysis based on molecular and process simulation

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ABSTRACT

A COSMO-based/Aspen Plus multiscale simulation methodology was used to evaluate a wide variety of ionic liquids (ILs), more than 300, as potential acetylene absorbents. First, by means of Conductor-like-Screening Model for Real Solvents (COSMO-RS) method, molecular simulations were conducted to select ILs with adequate thermodynamic (Henry's law constants) and kinetic (diffusion coefficients) properties as acetylene absorbents, using N,N-dimethylformamide (DMF) as benchmark industrial solvent for such solute absorption. Then, the operating units of acetylene absorption of an acetylene and argon mixture, and exhausted solvent regeneration were modeled in Aspen Plus. Simulations of absorption column using equilibrium based design model demonstrated that at least two ILs (1-butyl-3-methylimidazolium cation and acetate and sulfonate anions) present competitive solvent performance in acetylene absorption respect to DMF. In contrast, process analyses with a more realistic rate-based column model revealed that the mass transfer rate clearly controls the acetylene absorption with ILs compared to DMF, due to their viscosity differences. Finally, modeling solvent regeneration stage showed clear advantages of using ILs as acetylene absorbents since efficient acetylene recovery is achieved by flash distillation (vacuum pressure and temperature increase), operation hindered in the case of DMF due to is high volatility, requiring the solvent regeneration by a distillation equipment with higher operating and investment costs. Current COSMO-based/Aspen Plus approach has been demonstrated useful to perform preliminary analyses of the potential application of ILs in new separation processes, before starting with experimental essays, highly demanding in cost and time.

1. Introduction

Acetylene (C_2H_2) is an important organic raw material used in different industrial applications such as soldering or illumination and heat source [1]. The low yield of acetylene synthetized (between 5 and 30% of the total acetylene commercialized) in the chemical industry (by cracking naphtha or natural gas and plasma pyrolysis of coal) makes its separation and purification necessary [2]. The acetylene produced is accompanied with ethylene (C_2H_4), an essential chemical compound in the production of polymers such as polyethylene [3]. The presence of acetylene in the polymerization reactions of ethylene is undesired, since it can produce the catalyst poisoning influencing directly in the quality of the product [4]. Furthermore, during the polymerization reactions, an explosion can happen if acetylenic compounds are converted into solids and block the fluid stream. For these reasons, it is important to eliminate efficiently the acetylene from the ethylene feed streams [5]. The removal of acetylene from ethylene streams is commercially carried out by partial hydrogenation of acetylene over a supported noble metal catalyst such as Pd [6]. This process presents some disadvantages like the potential production of ethane by overhydrogenation of acetylene, causing the loss of the desirable reactive (ethylene). In addition, Pd catalyst can be deactivated by the formation of carbonaceous deposits, directly affecting the economy of the process. Physical separation by absorption using an organic solvent is an alternative commercial process used for the separation of acetylene [7]. Traditional organic absorbents, like N,N-dimethylformamide (DMF) and N-methylpyrrolidinone (NMP), present some typical disadvantages such as absorbent loss, difficult regeneration due to organic solvents' volatility and environmental pollution. For these reasons, big efforts have been focused on looking for new environmentally friendly solvents that overcome these disadvantages. In this sense, ionic liquids (ILs) have received attention as potential new solvents for gas separation processes [8]. The interest of using ILs to the task comes from their good properties: high and tunable solvent capacity, very low-vapor pressure, non-flammability, relatively high chemical and thermal stability and low corrosivity [8,9]. An additional peculiarity of ILs is that they are known as "designer

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solvents" since the cation and anion can be modified/permuted to design an IL with specific properties for a particular application [10]. Several groups have centered their research on the application of ILs as absorbents in different gas separation processes [11–13] including several solutes as CO_2 [14–17], NH_3 [18–21] or volatile organic compounds (VOCs) [22,23]. Several experimental studies have demonstrated that ILs present a wide range of mass absorption capacity depending on both their cation-anion chemical properties and molecular weights. In addition, it was reported that an important mass transfer kinetic control might occur in the absorption process using ILs [24], especially considering that these solvents present relatively high viscosity compared to conventional solvents. Recently, experimental and theoretical studies on the gas separation of C_2H_2/C_2H_4 by ILs have also been reported [13,25–29]. In those works, solubility measurements of acetylene in ILs of imidazolium or pyrrolidinium families with different anions have been carried out, obtaining higher capacities for acetylene absorption than those of traditional organic solvents [26]. It was experimentally demonstrated that the acetylene solubility increases in the IL with a stronger hydrogen-bond-acceptor (HBA) character [25,26]. Molecular dynamics studies also investigated the behavior of acetylene-ILs mixtures, comparing the theoretical and experimental results [27,28,30]. In a recent study, Zhao et al [29] used the Conductor-like-Screening Model for Real Solvents (COSMO-RS) method to predict the Henry's constants of acetylene and ethylene in ILs. In general, it was concluded that ILs with hydrogen bond acceptor groups are promising candidates to selectively separate acetylene, at least from a thermodynamic point of view.

Recently, our group has developed a multiscale research strategy oriented to develop new gas capture processes based on ILs systems [22,31], based on molecular simulation, experimental tests, and process simulation. In the first stage, COSMO-RS a priori computational method [32] is applied to obtain a preliminary selection of ILs with favorable thermodynamic/kinetic properties for the absorption of the required solute, minimizing the long and difficult experimental studies. Thus COSMO-RS method is applied to perform systematic screenings of Henry's law constants of gas solutes in ILs, among a huge database of ions (more than 500), to evaluate the cation and anion effect on the gas–liquid equilibrium (GLE) of the system. In addition, the intermolecular interactions in the fluid mixture can be analyzed by COSMO-RS, providing a guide for the selection of ILs with improved characteristics for the task. In the second stage, experimental absorption tests are carried out at different temperatures and pressures; employing a high-pressure microbalance, with the aim of evaluating the thermodynamics and kinetics of gas absorption in ILs [14,17,24]. As a result, key parameters for the design of absorption columns at industrial scale are obtained, such as absorption capacities and diffusivities. In the last stage of multiscale research methodology, the gas separation processes based on ILs are modeled by using the Aspen Plus commercial process simulator, including both the absorption and solvent regeneration stages. For this purpose, an integrated COSMO-based/Aspen Plus approach is applied to create components that are not in Aspen's database, as it is the general case of ILs [33]. Once the ILs have been included in Aspen Plus's database, the individual separation operations and global processes involving ILs can be modeled, easily carrying out sensitivity analyses of different design variables [22,24,31,34–37]. One main contribution of using process simulation analyses in the development of potential applications of ILs is that it allows introducing new technical and economic criteria in the selection of optimized ILs for specific separations [38]. In addition, professional process simulators can be used to perform viability analyses of the technology based on ILs (through the estimation of energy consumptions, operating and capital cost, etc.) by comparison to available commercial technologies that use conventional solvents [24,34].

In this work, the potential application of ILs in the separation of acetylene by absorption is evaluated by means of COSMO-based/Aspen Plus multiscale research strategy. However, one main modification on

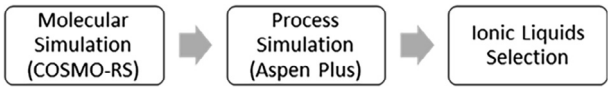

Fig. 1. Alternative multiscale research strategy diagram.

above described multiscale methodology is introduced: in this study, both molecular and process simulation are firstly and sequentially applied (Fig. 1) to preliminary select the ILs with better performance in the global gas separation processes. The use of the integrated molecular + process simulations allows performing a more rigorous selection of ILs from the view of the practical application at industrial scale, considering not only thermodynamic or kinetic properties but also technical, energetic and economic criteria. In addition, the performance of selected ILs is compared to that obtained using dimethylformamide (DMF), a conventional solvent industrially used to absorb acetylene. For this purpose, the COSMO-RS method is firstly applied to perform an IL property screening among a large database of ions (more than 300 ILs included). Henry's constant of acetylene in the IL solvent is predicted as thermodynamic parameter of reference to select ILs with high gas solute solubility, as it was successfully done previously [20,22]. The COSMO-RS approach is also used to estimate the viscosities for the calculation of the diffusion coefficient of acetylene in the studied ILs, by using Wilke-Chang model; i.e., molecular simulations also contribute to anticipating the kinetic behavior of the system. Additionally, COSMO-RS analysis allows better understanding the acetylene-IL mixture behavior from a molecular point of view, in terms of the intermolecular interactions happening in the fluid mixture. As a result, an initial selection of commercial ILs by means of thermodynamic and kinetic is carried out, comparing to the properties of DMF, which is used as benchmark industrial acetylene absorbent. Secondly, the unit operations for acetylene absorption and desorption are modeled using the selected ILs and DMF using the professional Aspen Plus process simulator. A sensitivity analysis of operating variables is carried out using rigorous equilibrium and rate-based models for the absorption operation in commercial packed columns, in order to evaluate the role of thermodynamics and kinetics in the separation efficiency. Lastly, the regeneration of the exhausted solvent is studied with a flash distillation, analyzing, for each solvent used, the temperature and pressure effect on the product purity and solvent losses. Current computational analysis contributes as a preliminary evaluation of the potential application of IL for acetylene absorption, as an alternative to the DMF conventional solvent, providing a set of ILs with favorable absorbent properties, contributing to minimize the number of experimental tests needed at laboratory or pilot plant scale.

2. Computational details

2.1. COSMO-RS calculations

Firstly, the geometry of gaseous compounds (acetylene and argon) involved in the work were optimized at BP86/TZVP computational level in gas phase. Two molecular models were used to describe de IL compounds: the ion-pair (CA) and the independent counter ions (C + A) models, optimizing the corresponding structures at BP86/TZVP computational level with solvent effect through the COSMO continuum solvation method. Once all the molecules were optimized until its minimum energy level, the polarized charge distribution on the molecular surface -obtained by a COSMO single point calculation- was saved in a .cosmo file. All these quantum-chemical calculations and .cosmo file generation were carried out in Turbomole 7.0 software. COSMOtherm program package (version C30_1501) and its parametrization BP_TZVP_C30_1501 was used, afterward, for the COSMO-RS calculations, obtaining the σ-profiles and σ-potentials of the pure compounds as well as the Henry's law constants of acetylene in ILs and detailed contributions to excess enthalpies in equimolar acetylene-IL