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Optimal Molecular Design of Ionic Liquids for High-Purity Bioethanol Production

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ABSTRACT: A mixed-integer nonlinear programming (MINLP) formulation for the molecular design optimization of ionic liquids (ILs) to recuperate ethanol with a purity of 99 mol % or greater from a E85 system (a mixture containing 85 and 15 mol % of ethanol and water, respectively) is presented. The reason why the ethanol/water separation is difficult is because of the azeotropic behavior of this system. Therefore, the IL is designed to feature water affinity such that it can break the ethanol/water azeotrope, allowing the high-purity separation to take place. The MINLP formulation is based on the development of a superstructure that contains a set of cations and anions, whose combination forms different kinds of ILs that have the potential to separate azeotropic systems such as the ethanol/water system. Because most of the ILs to be optimally designed are novel solvents, their physical and thermodynamic properties are estimated by group contribution methods. The optimization formulation is composed of a set of constraints featuring vapor–liquid equilibrium conditions as well as constraints dealing with structural and allowed cation–anion combinations. We assume that the separation will take place at atmospheric pressure. For the sake of simplicity, the optimal IL is first synthesized in a single separation stage, although the separation was also addressed using a reboiled absorption column. The results indicate that the optimally designed IL is capable of performing the required separation meeting the high-purity ethanol constraint.

1. INTRODUCTION

The supply of energy for various operations such as transportation, power generation, and heating is of critical concern in the world today. Fossil fuels like crude oil that have been the traditional source of energy are nonrenewable. Prices of fossil fuels like crude oil and natural gas have increased significantly in the past years. Moreover, today there is scientific evidence¹ that supports the claim that global warming problems are strongly related to the increase of the concentration of greenhouse gases mainly produced from the combustion of fossil fuels. This situation has led to a search for alternatives to fossil fuels. Therefore, the use and combination of alternative sources of energy like wind, solar, tides, geothermal, biomass energy, and fuel cells have the potential to meet the energetic demands of modern society featuring sustainable characteristics.

Regarding biofuels, there has been a renewed interest in the processing of biomass into fuels and chemicals via fermentation and gasification during the last years. In particular, research about efficient bioethanol production from cellulosic residues has been a very active research field in the past years.^{2,3} Historically, the main reason why ethanol has not been widely used either as a primary fuel or like an additive has to do with its high production cost. Moreover, the availability of corn has been limited by world food demands. Purifying an alcohol requires about 6% of the energetic value of the compound itself, with a large portion used in the separation of the alcohol from the fermentation broth, mainly composed of water.⁴ It has been estimated that the recovery of ethanol from fermentation broths is the most energy-extensive step in fermentative ethanol fuel production.⁵ In fact, the average energy requirement per liter of ethanol produced is 3594 kcal. To get an idea about the production cost in Oct 2009, the production cost of E85 was slightly smaller than

the corresponding production cost of regular gasoline per gallon.⁶ However, because the energy content of regular gasoline is higher than the energy content of E85 per gallon, the corresponding production cost of E85 was higher than the one reported for regular gasoline on an energy-equivalent basis. It must be stressed that E85 is not suitable for application either as a main fuel or as a gasoline additive. For this purpose, a high ethanol concentration, typically around 99.5%, is required. Therefore, increasing the ethanol purity from a E85 mixture will also increase its production cost. The situation turns out to be more complicated because of the presence of azeotropic behavior, which avoids the possibility that the separation takes place up to high ethanol purity. The only way ethanol finds its way into application as an alternative energy is by decreasing its production cost, making it competitive in comparison to fossil fuels. Therefore, one of the major hurdles in switching to a biomass-based industry is the production costs (both economic and energetic) of the base alcohols. Transportation is the other problem related to the wide use of ethanol as fuel because of piping corrosion problems. Traditionally, separating alcohols and water requires a series of distillation columns and solvents that tend to be dangerous for the environment. Moreover, this method is energetically expensive, and much room for improvement exists. For instance, the recent development of new membrane technology, such as pervaporation, has improved

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the efficiency of this separation, although rapid fouling of the membranes remains a major issue with these methods.⁷ Some other advances in separation technology has to do with the development of a new kind of green solvents, known as ionic liquids (ILs), that might be able to perform the required E85 separation up to high ethanol purity. It has been shown that ILs have the potential for separating alcohol/water mixtures with simple extractive distillation or liquid–liquid extraction.⁸

In this work, the separation of the E85 system will be addressed by using a new kind of green solvent (ILs). Solvents comprise two-thirds of all industrial emissions and one-third of all volatile organic compound emissions. In fact, “these emissions have been linked to a host of negative effects, including global climate change, poor urban air quality, and human illness”.⁴ The new constraints facing engineers are to continue to provide society with the products necessary for sustaining a high standard of living, while at the same time, significantly reducing the environmental impact of the manufacturing processes. Achieving these apparently contradictory objectives is one of the great challenges facing science and engineering in the coming decades. It is then apparent that new kinds of products (solvents) are required, and definitely those products must clearly feature sustainable characteristics. A new class of compounds, known as ILs, has emerged in the last years that may become a key ally in helping society meet the challenges of efficient and environmentally benign chemical processing. They have the potential to revolutionize the way we think of and use solvents. They act much like good organic solvents, dissolving both polar and nonpolar species. In many cases, they have been found to perform much better than commonly used solvents. Perhaps, the most intriguing feature of these compounds is that, while they are liquid in their pure state at room temperature, they have essentially no vapor pressure. They do not evaporate, and so they do not lead to fugitive emissions. Many of these compounds are liquids over large temperature ranges, from below ambient to well over 300–400 °C, which suggests they could be used under unique processing conditions.⁹

ILs consist of the assembly of large organic cations and inorganic or organic anions of smaller size and asymmetrical shape. These factors tend to reduce the lattice energy of the crystalline structure of the salt and hence to lower their melting point so that they generally remain liquid at or near room temperature. Unlike molecular liquids, the ionic nature of these liquids results in a unique combination of properties, namely, high thermal stability, large liquid-phase range, negligible vapor pressure, nonflammability, and high solvating capacity for organic, inorganic, and organometallic compounds, determining their high potential as “green solvents”.^{10,11} Furthermore, ILs can be considered as “designer solvents” because their physicochemical properties can be finely tuned by the proper choice of cations and anions. As a result, these solvents can be designed for a particular application and to feature a given set of intrinsic properties. However, presently ILs also feature some important disadvantages, among them we can cite the following ones: high manufacturing cost, toxicity, and corrosive action. Even when some of these indicators, such as toxicity levels,¹² could be diminished around safe values for the environment, the manufacturing cost is a clear shortcoming. From an industrial point of view, the most important properties of ILs are as follows: thermal stability, low vapor pressure, electric conductivity, tunable solubility (possibility for biphasic systems), liquid-crystal structures, high electroelasticity, high heat capacity, and inflammability.

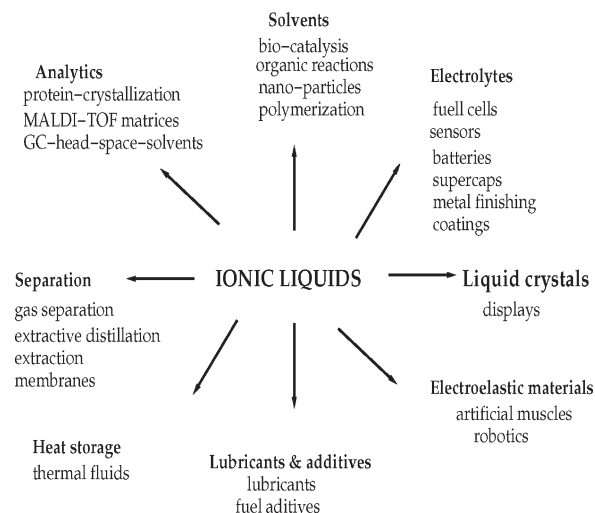


Figure 1. Selection of applications in which ILs have been used.

These properties enable the use of ILs in a wide range of applications, as shown in Figure 1. ILs have started to find their way into industrial applications. For instance, they have been used in bioprocesses such as the recovery of amino acids, processing of lignocellulosic materials, extraction of essential oils, extraction of organic acids, separation of polyphenolic compounds extracted from plant matrixes, extraction and recovery of azo dyes, separation of bioactive flavonoids, solvents for multiphase bioprocess operations, analysis of amino acids, and peptides and proteins in ILs, among others, which have been discussed in the literature. Zhao¹³ has reviewed some of the most important advances of ILs as versatile “green” engineering liquids in a variety of industrial applications including heat-transfer fluids, azeotrope-breaking liquids, lubricants, electrolytes, oil/water emulsion breakers, liquid crystals, supported IL membranes, and plasticizers, among others.

In many cases, the formation of azeotropes does not allow the separation of two or more compounds by simple distillation. However, sometimes the azeotrope can be broken by the addition of another compound. These compounds are called entrainers. ILs also act as entrainers for a great variety of azeotropic systems.^{14,15} Especially, if water is one component of the azeotrope, very high separation factors can be achieved. ILs usually are hygroscopic materials that show a strong affinity to water. Obviously, the interactions between the IL and water are much stronger than those between water and the other component of the azeotrope. The IL literally captures the water and releases the remaining compounds, which can be distilled off. In other words, the IL is acting as an extracting agent for water. The advantage of an IL over a classic entrainer is that ILs have extremely low vapor pressure, and if properly designed, they could feature low toxicity values. This means that the entrainer itself does not need to be distilled, and hence a second distillation column is not necessary and a significant amount of energy can be saved by using a simple evaporation process for IL/water separation.¹⁶

Current practice for new product design employs a trial-and-error process based on past knowledge and expertise.¹⁷ Moreover, although the designed product meets the required properties, there is no guarantee that the product is the best one in terms of its production cost. The development process for new product design can be shortened by the coupling of modeling and

optimization techniques. The idea is that, instead of trying many alternative formulations leading to a product meeting the associated constraint, only a small set of them could be identified and analyzed, reducing the experimental laboratory workload. In addition, the designed product would feature optimality characteristics. Specifically, in the case of the design of new molecules, the product design problem can be stated as “given the specifications of a desired product, determine the molecular structures of the chemicals that satisfy the desired product specifications”.¹⁸ However, because in some real situations reliable mathematical models can not be available for product design, it is probably true that a combination of trial-and-error and modeling—optimization techniques could render better results. Therefore, our aim in this work is to use modeling and optimization techniques to design molecular structures corresponding to a new kind of green solvents to perform the ethanol high-purity separation from E85 mixtures.

There are in the literature several works that address the problem of synthesizing novel molecular structures. Gani and Brignole¹⁹ proposed to synthesize molecular structures with specific solvent properties for the separation of aromatic and paraffinic hydrocarbons on the basis of UNIFAC predictions. In general, the number of molecular structures that can be obtained from the various groups is very large. An efficient computerized synthesis of compounds for the molecular design of solvents was developed. Brignole et al.²⁰ extended the Gani and Brignole¹⁹ work to include improved procedures for solvent synthesis, solvent evaluation, and solvent screening. Macchietto et al.²¹ presented a systematic procedure to aid the selection of physical solvents for liquid–liquid extraction and gas absorption processes. A mathematical optimization problem is formulated, and the optimal solvent or solvent mixture is found by selecting the number and type of structural groups in the solvent molecule, subject to chemical feasibility and engineering constraints. Odele and Macchietto²² used a mixed-integer nonlinear programming (MINLP) technique to solve the problem of selecting a solvent or solvent mixture with desirable combination of physical properties, yielding compounds with optimum values of appropriate performance indexes, subject to material balances, process and design limitations, and feasibility of molecular structures. Maranas²³ presented a systematic analysis framework for transforming a class of optimal computer-aided molecular design problems with nonlinear structure–property functionalities into equivalent mixed-integer linear programming (MILP) problems. Two alternative design objectives are considered: (i) minimization of the scaled deviation of design properties from some target values and (ii) minimization/maximization of a single property subject to lower and upper bounds on the rest of the properties. The framework is applied to the polymer design. Giovanoglou et al.²⁴ presented a mixed-integer dynamic optimization (MIDO) framework for solvent design in batch processes. The algorithm is based on decomposition of the MIDO primal subproblem into several steps that are solved successively. This decomposition allows unsuitable solvents to be detected and discarded quickly and without significant computational cost. The algorithm is applied successfully to an industrial case study dealing with a three-phase dehydration column and a decantation unit for solvent recovery (water/dimethylacetamide). Yang and Song²⁵ proposed a new algorithm, the classified enumeration, to solve computer-aided molecular design problems of solvents for separation processes. In this method, all groups are sorted into two parts: skeleton groups and function groups. The former can

constitute alkane, arene, or cycloalkane; the latter are the remainder. The skeleton groups are combined to form molecules as the base by enumeration. The function groups replace the corresponding skeleton groups in the molecule of the base to build other molecules. The properties of all acquired molecules are calculated using group contribution methods to find the proper solvents for the separation process. The method is used for the design of solvents for the removal of phenol from water, acetic acid from water, benzene from cyclohexane, and methanol from acetone. The difference between the mentioned works and the present one is that the previous works used molecular structural groups, considered the kind of bond, valence, octet rule, and others to define the solvent or polymer optimum molecular structure, and in this work, to select the IL, we use cations and anions that are conformed by specific molecular groups; as a consequence, the structural feasibility constraints change. We should stress that because in this work physical and equilibrium properties are computed by group contribution methods the range of cations and anions that can be considered for synthesizing ILs is limited to those components for which structural information is available.²⁶

The paper outline is as follows. In section 2, the problem description is addressed. In section 3, the solution methodology is described. In this part, we also discuss the criteria used for the selection of cations and anions that compose ILs. In section 4, the MINLP problem used for the optimal molecular design of the IL is formulated, whereas in section 5, the results and performance of the optimally designed IL are discussed. Finally, section 6 contains the conclusions of the work.

2. PROBLEM FORMULATION

The addressed research problem can be formulated as follows: “Given an initial set of properly selected cations and anions, the objective is to design the best molecular structure of an IL, formed as a proper combination of cations and anions, which is capable of breaking the ethanol–water azeotrope, allowing to obtain high purity ethanol demanded for bio-fuel applications.”

To address the solution of this problem, the following assumptions have been made:

- (a) On the basis of our experience and the literature about the performance of ILs,^{27–30} we made an initial screening of those cations and anions that are well suited for high-purity ethanol recovery from E85 mixtures.
- (b) An important requirement to selecting a family of cations and anions relates to the fact that they should exhibit water affinity and feature strong thermal stability. Water affinity guarantees that the IL may form a homogeneous phase with water and ethanol. On the other hand, the thermal stability constraint guarantees that the IL does not decompose over a large temperature interval. Moreover, the IL should feature a low vapor pressure, and as a consequence, such an IL does not evaporate at an appreciable extent.
- (c) An advantage of using ILs to carry out the separation of ethanol/water mixtures is that the separation is based on the preference of the IL to capture water molecules. Therefore, the presence of the IL modifies the vapor–liquid phase behavior between ethanol and water mixtures, removing the azeotrope that under normal circumstances is formed and that avoids high-purity ethanol

recovery. Moreover, the use of ILs may reduce the energy required to accomplish such a separation.

- (d) Because during optimal synthesis of the IL several combinations of cations and anions will give rise to nonexisting ILs, the physical and thermodynamic properties of the ILs will be calculated using a group contribution method.^{31,32} In particular, the nonideal behavior of the liquid phase is represented by the UNIFAC method.³³ Moreover, because we have assumed that the separation will take place at atmospheric conditions and that the IL is considered as a nondissociated component, the vapor phase will be treated as an ideal gas.
- (e) Because the aim of using ILs is to break the ethanol/water azeotrope, we assume that a previous distillation column has been used to reach the azeotropic composition (E85) under atmospheric pressure. Next, a reboiled absorption column using the optimally designed IL will be used to obtain high-purity ethanol. Normally, in a fermentation process, very dilute ethanol/water mixtures (3–7% ethanol mole fraction) are obtained. Therefore, a common practice is to get rid off the water by using a conventional distillation column until a E85 mixture is obtained. In this work, we assume that the separation will start from a E85 mixture.
- (f) For the sake of simplicity, the optimal synthesis of the IL to carry out the ethanol/water separation will be formulated using a single extraction stage. We have decided to concentrate our initial efforts in proposing an optimal IL formulation capable of performing the high-purity recovery of ethanol from ethanol/water mixtures.
- (g) In this work, we use a reboiled absorption column to carry out the ethanol/water separation up to high ethanol purity and to test the feasibility of the separation. The ethanol/water mixture forms a homogeneous mixture, meaning that a simple distillation column should be enough to carry out such a separation. The justification for carrying out the separation in a reboiler absorption column is due to the fact that we need to promote vapor–liquid contact through the column. The product (ethanol) was separated in the vapor phase. Of course, a condenser can be used to obtain liquid-phase ethanol. Other options that were also considered were extractive columns and heterogeneous distillation. However, these equipment are more suitable for performing liquid–liquid–vapor separations. We should mention that the capital cost inversion may be smaller in comparison to other separation schemes. For instance, other separation schemes that have been used to carry out the ethanol/water separation require a conventional distillation column coupled with a set of membrane modules,^{34,35} pressure-swing distillation columns,^{36,37} and wall-divided distillation columns.^{38,39} There are some other more conventional separation schemes that use heat-integrated distillation columns and posterior processing using membranes.⁵ We claim that using proper ILs the high-purity separation of the ethanol/water mixture can be done in a single reboiled absorption column working under atmospheric pressure and featuring green solvents and potential savings in both capital and operation costs. Of course, this claim should be verified because, in practice, the synthesis of ILs may be expensive. It is probably true that the performance of the IL also depends upon the design of the processing equipment in which the requested ethanol/

water separation will take place. In future work, we will address the simultaneous synthesis of the IL and the reboiled absorber column.

3. METHODOLOGY

In this section, the methodology for the optimal design of ILs aimed at separating the ethanol/water azeotropic mixture up to high purities will be discussed. The details of the optimization mathematical formulation will be given in the next section. Moreover, the criteria for the selection of the family of cations and anions that will be composed of the ILs will also be discussed.

In the design of new products, the physical and thermodynamic properties of such compounds can be tuned to meet a set of desired properties. Among these properties, the designer may be interested in a product featuring certain target values of properties such as vapor pressure, density, viscosity, thermal conductivity, etc. Commonly, the designer selects an experimental approach, leading to the discovery of the desired product. In this case, the designer normally starts to select a set of raw material substances and experimental conditions that hopefully will give rise to a compound featuring the requested properties as much as possible. However, the number of combinations of raw material substances together with the experimental conditions may demand excessive time and effort to obtain the desired compound.

An alternative approach to obtaining a product with target properties consists of formulating the product design problem as an optimization problem. Here the idea is to select a given set of raw material substances and to let the optimizer assemble a product that features the specified properties in the best possible way, subject to meeting a set of constraints. Of course, such an approach is not new, and it has been successfully used for the optimal design of polymer compounds,² solvents,² and agrochemical products,⁴⁰ among others. However, the optimization approach for the molecular design of new products should not be seen as a panacea because it is based on some assumptions that may not always hold. A disadvantage of this approach lies in the fact that, because the product to be designed actually does not exist, the physical and thermodynamic properties needed to simulate the behavior of the product will not be available. The way to overcome this difficulty has been through the estimation of the desired properties by group contribution methods.^{41,42} A drawback of these types of estimation methods is that they are not always reliable. They should be taken just as a practical way to obtain the value of the desired physical and thermodynamic properties when other estimation methods are not available. Moreover, the estimation of the physical properties by group contribution methods assumes that the values of the functional groups for the computation of a given property of the new product are readily available. This fact clearly limits the number of products that can be designed. A rigorous way to compute the properties of new compounds should be to use an *ab initio* approach⁴³ where the determination of the properties is done by performing quantum mechanics calculations. However, presently the computational load for carrying out an *ab initio* determination of the physical properties in an optimization framework seems to be well beyond the current computational facilities offered by serial computers. Other problems related to the optimal molecular design of new products deal with the optimization complexity of the design problems. Because integer

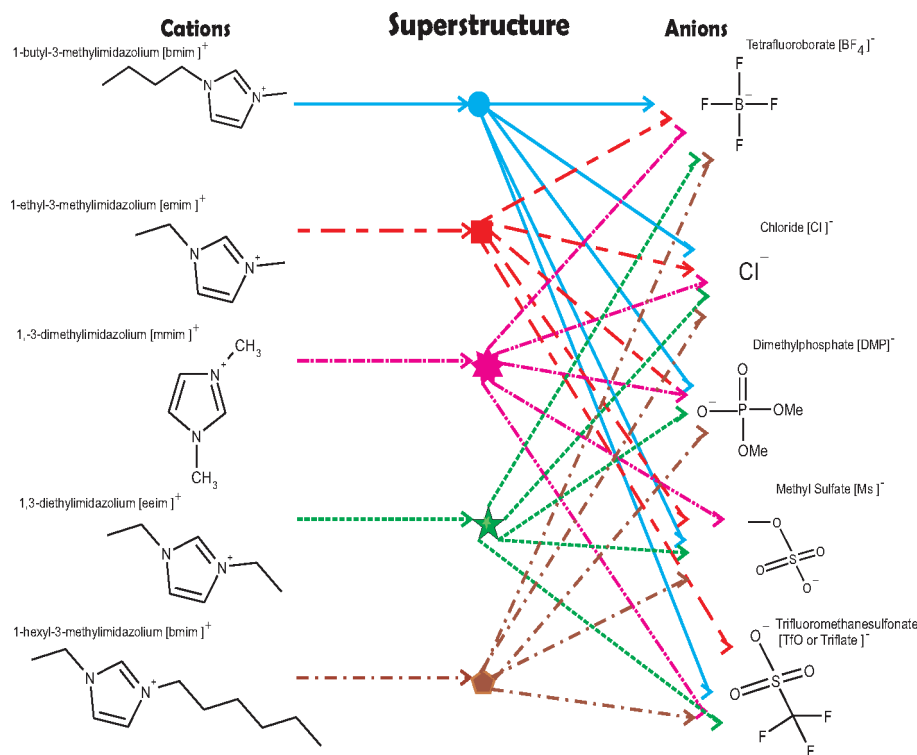


Figure 2. Family of cations and anions used for the optimal molecular design of the IL and superstructure representation of the allowed cation and anion combinations.

and continuous decision variables are involved, the underlying optimization problem will be a mixed-integer nonlinear program. Moreover, if the optimal molecular design also features dynamic behavior, the problem will be a MIDO problem. Both problems may be difficult to solve. In fact, even finding a feasible solution of such problems may be a challenge.

Because ILs are formed by a set of cations and anions and the number of potential candidates for forming the target IL may be large (in fact, it has been estimated that at least a million binary ILs and 10^{18} ternary ILs are potentially possible⁴⁴), an initial screening of the most promising cations and anions was made. Later in this section, we discuss some of the properties that cations and anions should feature to address the separation of the ethanol/water azeotropic mixture. We should stress that for the sake of simplicity we decided to start with a set of cations and anions instead of a family of functional groups from which the cations and anions may be assembled. This was done to keep the optimization problem as simple as possible with few binary decision variables. Accordingly, Figure 2 displays the cation and anion family that was used for the optimal molecular design of the IL. In this figure, a superstructure representation of all of the possible combinations of cations and anions is also shown. To choose the anion and cation of the IL, we make use of binary variables, which have two functions: (1) the selection of the anion and cation, which form the IL, and (2) the definition of the functional groups and group interaction parameters, which are used in the UNIFAC group contribution method. The UNIFAC method was used to determine the activity coefficients because there are interaction parameters and group volume and surface area parameters reported for some ILs in the literature.³

Having selected the cation and anion family to form the target IL, the next step consists of formulating an optimization problem

whose solution will provide the IL. In the next section, we discuss in detail the proposed optimal molecular design formulation, which includes the objective function, constraints, and both physical and thermodynamic property estimation methods. After the optimal design of the IL, the next step consists of checking by simulation that the selected IL performs the separation of the ethanol/water mixture beyond the azeotropic composition. In fact, regulations dictate that, to use ethanol as a biofuel in the transport sector, it should be almost anhydrous ethanol (99.5% or higher mole fraction). After considering several separation options, we came to the conclusion that a reboiled absorption column was enough to carry out the separation.

Criteria for Cation/Anion Selection. Even when, in principle, a large number of cations/anions can be selected, only a few of them feature desirable characteristics for the design of ILs aimed at breaking the azeotropic behavior of the ethanol/water system. In this section, we discuss in detail such relevant characteristics.

Chemical Stability. An IL is considered to be chemically stable when it does not react or decompose under reaction conditions. Until now, imidazolium-based ILs have been the most studied and used. Research has shown that most imidazolium-based ILs withstand acidic conditions but not basic ones.⁴⁵ The reason is the acidic proton at the carbon atom between nitrogen atoms in the imidazolium ring. Even a mild base can remove it and decompose the IL. The chemical stability toward bases slightly increases when this carbon atom is alkylated. When higher stability is needed, phosphonium-based ILs are a good choice because they are compatible even with strong bases.⁴⁶

Water Solubility. The increase of the length of an alkyl chain tends to decrease the water solubility by increasing the hydrophobicity of the cation.¹ If the IL has hydrophilic stability, it

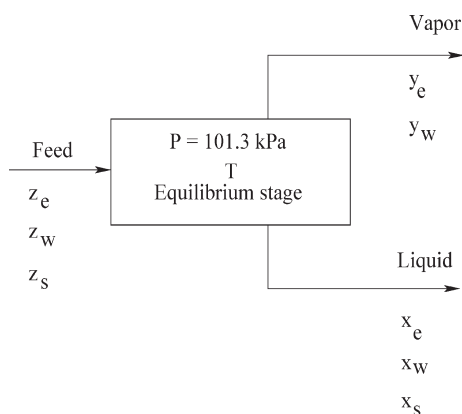


Figure 3. Equilibrium stage for the optimal molecular design of the IL to carry out the ethanol/water separation. Note that the vapor pressure of the IL is negligible.

avoids decomposition at operation conditions. Imidazolium-based ILs with benzene rings are difficult to dissolve in water. Regarding the solubility of some anions, the choice of the anion is one of the factors determining the solubility of the IL with water. At room temperature, all $[C_n\text{mim}][\text{PF}_6]$ and $[C_n\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ILs are insoluble in water, and all halide (Br^- , Cl^- , I^-), ethanoate ($[\text{CH}_3\text{CO}_2]^- = \text{OAc}^-$), nitrate ($[\text{NO}_3]^-$), and trifluoroacetate ($[\text{CF}_3\text{CO}_2]^-$) based ILs are fully water-soluble. However, ILs based on $[\text{BF}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ are positioned somewhere in between. Depending on the alkyl chain length on the cation, they either are fully miscible with water (e.g., $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$) or form biphasic systems ($[\text{C}_n\text{mim}][\text{BF}_4]$, $n > 4$). Thus, the anion has a primary effect on the water miscibility and the cation a secondary one.¹ Moreover, dimethylphosphate (DMP) was chosen because it forms ILs with imidazolium cations; the resulting IL is hydrophilic. This means that the DMP cation forms water-soluble low-density ILs.²⁸ Therefore, the synthesized solvents can be used in low-pressure distillation columns. In addition, as was previously mentioned, ILs featuring DMP and imidazolium are good solvents for ethanol/water azeotropic separations.

Viscosity. The IL viscosity is the main criterion for cation and anion selection because it determines the rate of heat- and mass-transport processes. It strongly affects the pumping, mixing, and agitation operations.⁴⁷ Alkyl chain lengthening or fluorination makes the salt more viscous because of an increase in the van der Waals interactions and hydrogen bonds.⁴⁸ Alkyl chain ramification increases the viscosity because of reduced rotation freedom.⁴⁹

Melting Temperature (T_m). The melting temperature generally decreases with an increase in the anion radius, except for $[\text{PF}_6]^-$. This is so because the larger anion radius induces weaker electrostatic interaction with the imidazolium cation.⁵⁰ The IL melting temperature has to be below the system operation temperature to guarantee the liquid state during the separation. Methylation at C_2 increases the melting point; for example, the melting point of 1-ethyl-2-methylimidazolium chloride is 454.15 K, which is much higher than that of 1-ethyl-3-methylimidazolium chloride (360.15 K); this implies that the effect of the van der Waals interaction via a methyl group dominates over the electrostatic interaction via a proton on C_2 .⁵¹ The melting point decreases as the length of the cation alkyl chain increases.⁵² ILs with symmetric cations exhibit the highest melting points; the

Table 1. Parameters and Decision Variables Used in the MINLP Model

binary variables	continuous variables	parameters
σ_m	y_j	$P, F, T_{\text{eb}}^{\text{H}_2\text{O}}$
α_m	T	z_j, a_{nm}
λ_k	$T_{\text{eb}}^{\text{IL}}$	$\Delta T_{\text{mp}}, \Delta T_{\text{eb}}$
	$T_{\text{mp}}^{\text{IL}}$	$\Delta T_{\text{mp},j}, \Delta T_{\text{mp},j}$
		$A_{\text{H}}, B_{\text{H}}, C_{\text{H}}, D_{\text{H}}, Z_{\text{H}}$
		$G_{m,1}, G_{m,2}$
		R_k, Q_k

melting points appear to fall steadily with an increase in the alkyl chain length. The ILs of imidazolium containing symmetric cations, such as 1,3-dimethylimidazolium, 1,3-diethylimidazolium, 1,2,3-trimethylimidazolium, and 1,2-dimethyl-3-ethylimidazolium, show higher melting points than those containing asymmetric cations.⁵³

Imidazolium-Based Cations. Methylimidazolium-based ILs are favorable to investigation because (a) they are stable in water and air, (b) they remain in the liquid phase for wide temperature ranges, (c) they remain liquids at room temperature, and (d) they have relatively favorable viscosity and density characteristics.⁵⁴

4. MINLP PROBLEM FORMULATION

To carry out the optimal molecular design of the IL, we will assume that the separation of the ethanol/water azeotropic system will take place in a single separation stage shown in Figure 3 (all variables are described in the Nomenclature section). Given the objective function, the set of constraints, and the optimization variables, the aim of this work is to carry out the optimal molecular design of ILs to recuperate ethanol with purity 99 mol % or greater from a E85 system (a mixture containing 85 and 15 mol % of ethanol and water, respectively). All variables are defined in the Nomenclature section. Table 1 contains a detailed list of both the parameters and decision variables.

Objective Function.

$$\min_{x_{ij}, y_{ij}, T, L, V, T_{\text{eb}}, T_{\text{mp}}} f = (y_e^s - y_e)^2 \quad (1)$$

In the above objective function, y_e stands for the ethanol mole fraction purity and y_e^s is the desired ethanol mole fraction. The objective function simply states our target design goal: the optimal IL should allow ethanol/water separation up to high purities. To achieve this aim, we would normally set $y_e^s \geq 0.995$. The remaining variables $x_{ij}, y_{ij}, T, L, V, T_{\text{eb}}$, and T_{mp} are the liquid-phase mole fraction, vapor-phase mole fraction, stage temperature, liquid flow rate, vapor flow rate, boiling point temperature, and melting point temperature, respectively.

Continuous Constraints. • Total mole balance

$$F = V + L \quad (2)$$

where F, V , and L are the flow rates of the main feed stream and vapor- and liquid-phase streams, respectively.

• Component mole balance

$$Fz_e = Vy_e + Lx_e \quad (3)$$

$$Fz_w = Vy_w + Lx_w \quad (4)$$

$$Fz_s = Lx_s \quad (5)$$

where z is the composition of the feed stream, y is the vapor-phase composition, and x is the liquid-phase composition. The subscripts e, w, and s stand for ethanol, water, and IL, respectively. An important characteristic of the ILs is that their vapor pressure is almost negligible. Therefore, we can safely assume that the IL will only be present in the liquid phase. This is the reason why, in the IL individual mole balance, no IL is present in the vapor phase.

- Equilibrium relationships

The vapor phase is supposed to be an ideal gas. This is because we assume that the separation operation will be carried out at low pressure (1 atm). As a consequence, the fugacity coefficients Φ_i are set equal to 1. However, because the liquid phase is composed of polar, alcohol, anion, and cation compounds, the liquid phase will form a nonideal liquid mixture. Nonidealities in the liquid phase will be modeled through activity coefficients γ_i . The equilibrium equations are

$$x_e P_e^\circ \gamma_e = y_e P \quad (6)$$

$$x_w P_w^\circ \gamma_w = y_w P \quad (7)$$

where P° is the vapor pressure and P is the separation pressure.

- Vapor pressure⁵⁵

$$\ln\left(\frac{P_e^\circ}{P_{e,c}}\right) = (1 - X_e)[VP_A^e X^e + VP_B^e (X^e)^{1.5} + VP_C^e (X^e)^3 + VP_D^e (X^e)^6] \quad (8)$$

$$\ln\left(\frac{P_w^\circ}{P_{w,c}}\right) = (1 - X_w)[VP_A^w X^w + VP_B^w (X^w)^{1.5} + VP_C^w (X^w)^3 + VP_D^w (X^w)^6] \quad (9)$$

where

$$X^e = 1 - \frac{T}{T_{e,c}}; \quad X^w = 1 - \frac{T}{T_{w,c}} \quad (10)$$

- Activity coefficients (UNIFAC)³

Because we assume that the IL is a new product, for which no experimental physical property information is available, a group contribution method should be used to estimate the activity coefficients. Group contribution methods are aimed at computing some required properties starting from simple functional groups. By selecting the proper functional groups, we can design a product with target properties. The UNIFAC method is a reliable technique for activity coefficient estimation³ and is given as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (11)$$

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - S q_i \left[1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right] \quad (12)$$

$$F_i = \frac{q_i}{\sum_j q_j x_j}; \quad V_i = \frac{r_i}{\sum_j r_j x_j} \quad (13)$$

$$r_i = \sum_k \nu_k^{(i)} R_k; \quad q_i = \sum_k \nu_k^{(i)} Q_k \quad (14)$$

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (15)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m (\theta_m \psi_{km}) / \sum_n \theta_n \psi_{nn} \right] \quad (16)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_i \nu_m^{(i)} x_i}{\sum_i \sum_k \nu_k^{(i)} x_i} \quad (17)$$

$$\psi_{nm} = \exp[-(a_{nm}/T)] \quad (18)$$

As was previously mentioned, all of the terms are defined in the Nomenclature section.

- Mole fraction summation

$$y_e + y_w = 1 \quad (19)$$

$$x_e + x_w + x_s = 1 \quad (20)$$

These constraints enforce that the vapor and liquid mole fractions always add to unity.

- To enforce breaking of the ethanol/water azeotrope

The constraint to ensure that the resulting mixture does not exhibit azeotropic behavior reads as follows:

$$y_e \geq x_e + x_s \quad (21)$$

The justification of this equation comes from the fact that we need to guarantee that the optimally designed IL is capable of carrying out the separation of the ethanol/water mixture beyond the azeotropic composition point. Therefore, a constraint enforcing this behavior is needed. Equation 21 consists of two parts: (a) It implies that the ethanol vapor-phase mole fraction (y_e) must be higher than the corresponding equilibrium ethanol liquid-phase mole fraction (x_e). Without this condition, no ethanol mole fraction beyond the azeotropic point can be guaranteed. However, we recognize that the simple presence of the IL can lead one to think that the separation beyond the azeotropic point could be feasible without using eq 21, but actually this is not totally true (i.e., it may be true for certain kinds of ILs but false for others). Optimization techniques allow us to set the conditions such that, if an optimal and feasible solution exists, we can be sure that such a solution meets the stated conditions. Therefore, by including eq 21, we end up with a more robust optimization formulation that guarantees separation beyond the azeotropic composition point. (b) Equation 21 reduces to the well-known azeotropic composition condition in the absence of IL ($y_e = x_e$). Of course, this is what one gets by simple mass, energy, and equilibrium conditions (i.e., the separation beyond the azeotropic point cannot be attained). Moreover, this part of the constraint clearly states that the amount of IL used to carry out the ethanol/water separation is directly proportional to the difference between the target vapor-phase mole fraction and the liquid-phase azeotropic composition ($y_e - x_e \geq x_s$). Hence, as this difference grows, so does the amount of IL needed to perform the addressed separation task.

Table 2. Contributions of Simple Groups (*i*) for the IL Normal Boiling Temperature⁵

without ring		with ring	
group <i>i</i>	$\Delta T_{b,i}$	group <i>i</i>	$\Delta T_{b,i}$
–CH ₃	23.58		
–CH ₂ –	22.88		
>C<	18.25	=CH–	26.73
–O–, [–O] [–]	22.42	>N–, [>N<] ⁺	68.16
=O	–10.50	=N–, [>N=] [–]	57.55
–F	–0.03		
–Cl	38.13		
–P	34.86		
–B	–24.56		
O=S=O	147.24		

• IL normal boiling temperature

After carrying out the separation of the ethanol/water system, we need to deal with the separation of the resulting water/IL mixture. Because ILs are reported to be expensive liquids,⁵⁶ we need to maximize its recovery. To ensure an easy separation of the water/IL system, we can formulate a constraint stating that the boiling points of water and the IL be as far apart as possible.³ A simple way to achieve this aim is to formulate a constraint stating that the IL boiling point temperature ($T_{\text{eb}}^{\text{IL}}$) should be greater than the corresponding water boiling point temperature ($T_{\text{eb}}^{\text{H}_2\text{O}}$) plus a desired boiling point temperature approach (ΔT_{eb}) between both. The underlying constraint reads as follows:

$$T_{\text{eb}}^{\text{IL}} \geq T_{\text{eb}}^{\text{H}_2\text{O}} + \Delta T_{\text{eb}} \quad (22)$$

To compute the IL boiling point temperature, Alvarez and Valderrama⁵⁵ combined Lydersen's method with the Joback–Reid method to propose a “modified Lydersen–Joback–Reid” method that proved to give good results for molecules of high molecular weight. The proposed equation for computing $T_{\text{eb}}^{\text{IL}}$ reads as follows:

$$T_{\text{eb}}^{\text{IL}} = 198.2 + \sum_i (n_i \Delta T_{b,i}) \quad (23)$$

where n_i is the number of times that a group appears in a molecule and $\Delta T_{b,i}$ is the value of the contributions by the type of group *i* shown in Table 2.

• IL melting point temperature

To be sure that water and the IL can be separated and that the IL remains in the liquid phase, the IL melting temperature ($T_{\text{mp}}^{\text{IL}}$) must be lower than the difference between the system operation temperature (*T*) and a temperature approach (ΔT_{mp})³

$$T_{\text{mp}}^{\text{IL}} = T_{\text{mp}} \leq T - \Delta T_{\text{mp}} \quad (24)$$

where

$$T_{\text{mp}}^{\text{IL}} = \frac{\sum_k (N_k \Delta T_{\text{mp},k}) + z_{\text{H}} \sum_j (N_j \Delta T_{\text{mp},j})}{A_{\text{H}} + B_{\text{H}}\sigma + C_{\text{H}}\tau + D_{\text{H}}\delta} \quad (25)$$

The above equation is the group contribution model developed by Huo et al.³¹ to determine the melting point of imidazolium and benzimidazolium ILs. In ref 31, the melting point of an IL

is considered to be a function of the structurally dependent parameters, which are thereby determined by summing the frequency number of each group occurring in the molecule with its contribution.

Binary Constraints. In the proposed optimization formulation, binary variables enter in two kinds of constraints: (1) constraints to select anions, cations, and the IL and (2) constraints to define the type and number of functional groups in the IL, as well as to determine parameters of the UNIFAC group contribution method.

- Number of –CH₃ groups in the selected cation (n_1^s)

$$n_1^s = \sum_{m=1}^{N_c} G_{m,1} \sigma_m \quad (26)$$

where $G_{m,1}$ is the number of –CH₃ groups in the cation structure, σ_m is a binary variable to represent each cation *m* in the superstructure, and N_c is the number of cations. This equation quantifies the number of –CH₃ groups present in the cation of the selected IL. This quantity is added to the number of –CH₃ groups of the other compounds in the ethanol/water/IL mixture to obtain the fraction of –CH₃ groups in the mixture, which is used in the UNIFAC method.

- Number of –CH₂ groups in the selected cation (n_2^s)

$$n_2^s = \sum_{m=1}^{N_c} G_{m,2} \sigma_m \quad (27)$$

where $G_{m,2}$ is the number of –CH₂ groups in the cation structure. This equation quantifies the number of –CH₂ groups present in the cation of the selected IL. This quantity is added to the number of –CH₂ groups of the other compounds in the ethanol/water/IL mixture to obtain the fraction of –CH₂ groups in the mixture, which is used in the UNIFAC method.

- Only one cation should be selected

$$\sum_{m=1}^{N_c} \sigma_m = 1 \quad (28)$$

This equation guarantees the selection of only one cation of the superstructure to conform to the optimum molecular structure of the IL.

- Only one anion should be selected

$$\sum_{m=1}^{N_a} \alpha_m = 1 \quad (29)$$

where α_m is a binary variable to represent each anion *m* in the superstructure and N_a is the number of anions. This equation guarantees the selection of only one anion from the superstructure to conform to the optimum molecular structure of the IL.

- To determine if the selected cation contains the methylimidazolium (mim) group in its structure

$$\sigma_m + \alpha_j - \lambda_k \leq 1 \quad \forall \quad m = 1, 2, 3, 5 \\ j = 1, 2, \dots, 5; \quad k = 5, 7, 9, 11, 13 \quad (30)$$

Table 3. UNIFAC Group Parameters of Volume R_k and Surface Area Q_k ³³

no.	principal group	subgroup	R_k	Q_k
1	CH ₂	CH ₃	0.9011	0.8480
2	CH ₂	CH ₂	0.6744	0.5400
3	OH	OH	1.0000	1.2000
4	H ₂ O	H ₂ O	0.9200	1.4000
5	[mim][DMP]	[mim][DMP]	6.2609	4.9960
6	[mim][DMP]	[im][DMP]	5.3598	4.1480
7	[mim][CH ₃ SO ₄]	[mim][CH ₃ SO ₄]	3.7481	3.0714
8	[mim][CH ₃ SO ₄]	[im][CH ₃ SO ₄]	2.8470	2.2234
9	[mim][BF ₄]	[mim][BF ₄]	6.5669	4.0050
10	[mim][BF ₄]	[im][BF ₄]	5.6658	3.1570
11	[mim][Cl]	[mim][Cl]	5.7073	4.9741
12	[mim][Cl]	[im][Cl]	4.8062	4.1261
13	[mim][CF ₃ SO ₃]	[mim][CF ₃ SO ₃]	9.5357	5.0500
14	[mim][CF ₃ SO ₃]	[im][CF ₃ SO ₃]	8.6346	4.2020

where λ_k is a binary variable representing the k th combination of cations and anions in the superstructure.

• To determine if the selected cation contains the imidazolium (im) group in its structure

$$\sigma_m + \alpha_j - \lambda_k \leq 1 \quad \forall \quad m = 4$$

$$j = 1, 2, \dots, 5; \quad k = 6, 8, 10, 12, 14 \quad (31)$$

The surface area and volume parameters of the ionic pair of the ILs reported by Lei et al.³³ of the UNIFAC method are represented by a main group and two subgroups. The difference between the subgroups lies in the cation structure. The first one is the mim, and the second one is only im, while the anion is the same for both subgroups. Each subgroup presents different values of the volume (R_k) and surface area (Q_k). For this reason, it is relevant to identify the kind of subgroup that is present in the cation of the optimal structure of the IL. Equation 29 establishes that the selected cation to make the IL contains the mim subgroup. Equation 30 allows one to identify whether the selected cation has the im subgroup structure. The different cations in the superstructure only have one of these subgroups.

• Only an ionic pair should be selected

$$\sum_{k=5}^{14} \lambda_k = 1 \quad (32)$$

This equation enforces that only an ionic pair of the family is selected. The ionic pair is used in the method of UNIFAC. As stated in ref 33, “the ionic pair has strong electrostatic interaction and thus it is better to treat the skeletons of the cation and anion as a whole”, like, for example, [mim][DMP], [im][DMP], [mim][BF₄], [im][BF₄], and others.

• Number and type of ionic groups in the final IL

$$\lambda_k - n_k^s = 0 \quad \forall \quad k = 5, 6, \dots, 14 \quad (33)$$

$$\sum_{k=5}^{14} n_k^s = 1 \quad (34)$$

These equations identify the kind and number of ionic pairs present in the optimal molecular structure of the IL. The kinds of ionic pairs considered in this work are shown in Table 3, from rows 5 to 14.

• Superficial area of the final IL (Q^s)

$$Q^s - Q_k \lambda_k \leq 0 \quad \forall \quad k = 5, \dots, 14 \quad (35)$$

This equation assigns the surface area value of the ionic pair to the Q^s variable, which is employed in the determination of the fraction of the group surface area in the UNIFAC method.³

• Determination of the interaction parameter between the ionic part and the CH₃ group ($\Omega_k^{\text{ILCH}_3}$)

$$\Omega_k^{\text{ILCH}_3} - \Omega_{k,1} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (36)$$

This equation selects the UNIFAC interaction parameter corresponding to the group of the ionic pair present in the optimal molecular structure of the IL and the CH₃ group.

• Determination of the interaction parameter between the ionic part and the CH₂ group ($\Omega_k^{\text{ILCH}_2}$)

$$\Omega_k^{\text{ILCH}_2} - \Omega_{k,2} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (37)$$

This equation selects the UNIFAC interaction parameter corresponding to the group of the ionic pair present in the optimal molecular structure of the IL and the CH₂ group.

• Determination of the interaction parameter between the ionic part and the OH group (Ω_k^{ILOH})

$$\Omega_k^{\text{ILOH}} - \Omega_{k,3} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (38)$$

This equation selects the UNIFAC interaction parameter corresponding to the group of the ionic pair present in the optimal molecular structure of the IL and the OH group.

• Determination of the interaction parameter between the ionic part and the H₂O group ($\Omega_k^{\text{ILH}_2\text{O}}$)

$$\Omega_k^{\text{ILH}_2\text{O}} - \Omega_{k,4} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (39)$$

This equation selects the UNIFAC interaction parameter corresponding to the group of the ionic pair present in the optimal molecular structure of the IL and the H₂O group.

• Determination of the interaction parameter between the CH₃ group and the ionic part ($\Omega_k^{\text{CH}_3\text{IL}}$)

$$\Omega_k^{\text{CH}_3\text{IL}} - \Omega_{1,k} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (40)$$

$$\sum_{k=5}^{14} \Omega_k^{\text{CH}_3\text{IL}} = \Omega_1^{\text{OIL}} \quad (41)$$

The above equations select the UNIFAC interaction parameter corresponding to the CH₃ group and the group of the ionic pair (functional groups for UNIFAC) present in the optimal molecular structure of the IL.

• Determination of the interaction parameter between the CH₂ group and the ionic part ($\Omega_k^{\text{CH}_2\text{IL}}$)

$$\Omega_k^{\text{CH}_2\text{IL}} - \Omega_{2,k} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (42)$$

$$\sum_{k=5}^{14} \Omega_k^{\text{CH}_2\text{IL}} = \Omega_2^{\text{OIL}} \quad (43)$$

Table 4. UNIFAC Group Interactive Parameters a_{nm} , K (n Indicates the Row and m the Column)^{3,5}

		1, 2	3	4	5, 6	7, 8	9, 10	11, 12	13, 14
		CH ₂	OH	H ₂ O	[mim][DMP]	[mim][CH ₃ SO ₄]	[mim][BF ₄]	[mim][Cl]	[mim][CF ₃ SO ₃]
1, 2	CH ₂	0.00	986.50	1318.00	965.96	575.45	1108.51	2093.97	405.39
3	OH	156.40	0.00	353.50	9.67	13.83	−13.77		34.90
4	H ₂ O	300.00	−229.10	0.00	6617.00		242.88		40.42
5, 6	[mim][DMP]	180.41	−746−52	−1154.30	0.00				
7, 8	[mim][CH ₃ SO ₄]	473.80	−570.26	n.a.		0.00			
9, 10	[mim][BF ₄]	588.74	131.24	−408.00			0.00		
11, 12	[mim][Cl]	1129.01	n.a.	n.a.				0.00	
13, 14	[mim][CF ₃ SO ₃]	284.37	−305.24	−335.22					0.00

The above equations select the UNIFAC interaction parameter corresponding to the CH₂ group and the group of the ionic pair (functional groups for UNIFAC) present in the optimal molecular structure of the IL.

• Determination of the interaction parameter between the OH group and the ionic part (Ω_k^{OHIL})

$$\Omega_k^{\text{OHIL}} - \Omega_{3,k} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (44)$$

$$\sum_{k=5}^{14} \Omega_k^{\text{OHIL}} = \Omega_3^{\text{OIL}} \quad (45)$$

The above equations select the UNIFAC interaction parameter corresponding to the OH group and the group of the ionic pair (functional groups for UNIFAC) present in the optimal molecular structure of the IL.

• Determination of the interaction parameter between the H₂O group and the ionic part ($\Omega_k^{\text{H}_2\text{OIL}}$)

$$\Omega_k^{\text{H}_2\text{OIL}} - \Omega_{4,k} \lambda_k = 0 \quad \forall \quad k = 5, \dots, 14 \quad (46)$$

$$\sum_{k=5}^{14} \Omega_k^{\text{H}_2\text{OIL}} = \Omega_4^{\text{OIL}} \quad (47)$$

The above equations select the UNIFAC interaction parameter corresponding to the H₂O group and the group of the ionic pair (functional groups for UNIFAC) present in the optimal molecular structure of the IL.

• Determination of the molecular weight of the selected IL (MW_{IL})

$$\sum_{m=1}^S (MW_m^a \alpha_m + MW_m^c \sigma_m) = MW_{\text{IL}} \quad (48)$$

where MW^a and MW^c are the molecular weights of the anions and cations, respectively. This equation determines the molecular weight of the optimal molecular structure of the IL from the cation and anion. In the equations of this section, the numbers in the sets of the formulation are functional groups, and the subgroups of the UNIFAC group contribution method are shown in Table 3.

5. OPTIMAL MOLECULAR DESIGN

Commonly, the ethanol/water mixture obtained from fermentation reactors contains a low ethanol concentration (3–7% ethanol mole fraction). We assume that a conventional

Table 5. Contributions of the Simple Groups for the IL Melting Point Temperature³

without ring		with ring		ionic group	$\Delta T_{\text{mp},j}$
group	$\Delta T_{\text{mp},k}$	group	$\Delta T_{\text{mp},k}$		
−CH ₃	−0.4926				
−CH ₂ −	0.1324			[−O] [−]	−1.305
−O−	0.0835	=CH−	−1.497	[−B] [−]	−2.261
SO ₂	−1.0800	>N−	−13.85	[Cl] [−]	−3.300
>P=O	−0.9594			[=N<] ⁺	2.680
−F	0.1022				
>C<	−0.5317				

distillation column will be used to increase the ethanol purity from a low composition up to around the azeotropic composition (E85 mixture). To increase the ethanol concentration up to the high-purity region required for biofuel applications of ethanol, a reboiled absorption column will be used where the solvent or extracting agent will be taken as the optimally designed IL. We consider that, with ILs being expensive products, it makes more sense to use them only for the difficult part of the separation task.

Accordingly, two IL design scenarios were set up. In the first scenario, the proportion of the IL in the feed stream was taken as 20 wt %, whereas in the second design scenario, the proportion of the IL was 30 wt %. Of course, in practice the real proportion of the IL would depend upon the operating conditions of the separation process used to carry out the separation task. In this part, thermodynamic and related information used for solving the optimal molecular design problem are provided. The UNIFAC group interactive parameters a_{nm} , the contributions of the simple groups for the IL melting point temperature, the parameters used in the IL melting point temperature, and the number of CH₃ and CH₂ groups in the cations are provided in Tables 4–7, respectively. Moreover, the temperature gradients for the IL boiling point temperature (ΔT_{eb}) and the IL melting point temperature (ΔT_{mp}) are 15 and 10 K, respectively.

The strategy for solving the MINLP model of the IL molecular design problem consists of the following steps:

- 1 Establish good upper and lower bounds of the decision variables, according to problem knowledge and the thermodynamic behavior of the system.
- 2 Get good initial values for all continuous decision variables of the model by simulating a vapor–liquid equilibrium stage. Previous to the simulation, we chose an IL (i.e., select

Table 6. Parameters Used in the IL Melting Point Temperature³

parameter	value	parameter	value
A_H	-0.041 77		
B_H	0.004 665	D_H	0.005 428
C_H	-0.018 59	Z_H	2.355

a cation and an anion) and the operating temperature of the equilibrium stage. These data are not parameters in the molecular design optimization but decision variables. We use *Matlab* to simulate the equilibrium stage. In this step, the equations to be solved are given by eqs 2–20, making sure that eqs 22 and 24 are met.

- 3 Solve the relaxed MINLP model considering the information obtained in steps 1 and 2. The binary variables are treated as continuous variables (selection of the cation, anion, and IL resulting). The operating temperature of the equilibrium stage is now a decision variable. CONOPT⁵⁷ is the solver used for solving the underlying optimization problem.
- 4 Solve the MINLP problem using the information obtained in step 3 as the initial values and using the SBB solver. The solution of the MINLP problem is a local optimum of the IL molecular design problem.
- 5 Find the global optimum of the MINLP model using BARON⁵⁸ as the solver and using the information gathered in step 4 as the initial values.

We should stress that, from the step 3 and on, the entire MINLP model is considered in the solution of the IL design problem (from eq 1 to eq 48). One of the differences between the above steps is the solver used in each step and the sequential update of the initial values. We have found that this strategy allows one to improve the initial values of the continuous and discrete variables in each step in a systematic way, which makes it possible to find the solution of the different parts of the MINLP model until finally the global optimum is computed. The results of the IL optimal molecular design are shown in Table 8. Problem statistics are as follows: for both design scenarios, the number of constraints is 452, whereas the number of decision variables is 463. Regarding the CPU time, the first design scenario demanded 0.8 and 275 s using SBB and BARON, respectively, whereas the second design scenario demanded 1.3 and 316 s using SBB and BARON, respectively.

It can be appreciated that for the first scenario the IL formed by the combination between 1-ethyl-3-methylimidazolium dimethylphosphate [emim] and DMP is the selected IL and that a 94.6% ethanol purity recovery is reached in a single vapor–liquid equilibrium stage, whereas for the second design scenario, the selected IL is formed by the combination between 1,3-dimethylimidazolium dimethylphosphate [mmim] and DMP. With this product, a 94.7% ethanol mole fraction is reached, slightly better than the first one.

Because global optimal solutions were sought, it is clear that the synthesized IL corresponds to the best IL that one could find among all of the allowed combinations of cations and anions. To show this, we decided to synthesize a new IL featuring poorer separation characteristics. To do so, we proposed a new IL superstructure without taking into account the DMP compound as member of the anion family set. Accordingly, Table 9 presents the results when one forbids selection of the aforementioned

Table 7. Number of CH₃ and CH₂ Groups in the Cations

cation	$G_{m,1}$	$G_{m,2}$	cation	$G_{m,1}$	$G_{m,2}$
[bmim] ⁺	1	3			
[emim] ⁺	1	1	[eeim] ⁺	2	2
[mmim] ⁺	1	0	[hmim] ⁺	1	5

anion. In both design scenarios, the new IL selected is the same (1,3-dimethylimidazolium tetrafluoroborate, [dmim][BF₄]). As seen, the difference in the proportion of the IL fed to the equilibrium stage in both scenarios does not have any effect on the nature of the selected IL. In the first case, ethanol is recovered with a 92.0% mole fraction, whereas in the second case, 93.62% mole fraction is reached. As noted, in the last case, the IL is unable to get higher ethanol recovery compared to the optimal molecular design displayed in Table 8.

Regarding the feed stream composition of the IL, we recognize that this variable affects the final design of the IL. However, we consider that the composition of the feed stream of the IL has nothing to do with computing the chemical structure of the IL, which was our aim in trying to get an optimal IL to allow the ethanol/water separation task. This is the main reason why we decided to fix the feed stream composition of the IL, and we think this does not contradict the purpose of our work. By trial and error, we found that the feed stream IL compositions used in the two design scenarios meet the separation target. We consider that the feed stream composition of the IL is an operating variable, and it depends on the type of process used for carrying out the separation task.

After having designed an optimal IL featuring the potential for high-purity ethanol recovery, we checked that the IL could realize such a separation task by using a reboiled absorption column. We should recall that ethanol aimed as fuel in the transportation sector demands high purities of at least 99% mole fraction. For this aim, we simulated the ethanol/water azeotropic separation featuring the IL previously designed in a reboiled absorption column, whose flowsheet is shown in Figure 4. The IL is fed into one extreme of the column, whereas the ethanol/water mixture is fed somewhere between the column extremes. On one extreme of the column, we obtain high-purity ethanol, whereas in the other extreme, water and the IL ionic, with traces of ethanol, are obtained. The column works at atmospheric pressure conditions. We do not claim that the column works at optimal operating conditions; our objective was just to demonstrate the feasibility of carrying out the ethanol/water azeotropic separation using ILs. The flow rate, pressure, temperature, and mole fractions of the feed stream ethanol/water are 0.9557 kmol/s, 1 atm, 358.9 K, and 0.85 and 0.15, respectively, whereas the IL flow rate, pressure, and temperature are 0.0443 kmol/s, 1 atm, and 355.3 K, respectively.

Accordingly, for running the reboiled absorption column steady-state simulations, we used the IL that gives rise to the greatest ethanol recovery. We changed the number of equilibrium stages to learn what impact such a change has on the ethanol purity recovery. Therefore, three processing schemes were analyzed: (1) three equilibrium stages; (2) five equilibrium stages; (3) nine equilibrium stages. Table 10 shows the results of the simulations. It can be observed that, as the number of equilibrium stages increases, the ethanol purity also increases, until 99.96% mole fraction. Therefore, the results indicate that it is possible to reach high purity ethanol purification.

Table 8. IL Molecular Design Results^a

		composition							
design scenario	compound	feed wt fraction	equilibrium		ratio of IL in the global feed (wt %)	operation temperature (K)	some characteristics of selected IL		
			liquid mole fraction	vapor mole fraction			melting temperature (K)	boiling temperature (K)	molecular weight
(1)	ethanol	0.749 70	0.762 85	0.946 4	20	368.1	293.8	612.9	236.2
	water	0.051 74	0.178 73	0.053 6					
	IL	0.198 56	0.058 42						
(2)	ethanol	0.654 81	0.723 90	0.947 44	30	375.2	320.1	590	222.2
	water	0.045 19	0.172 33	0.052 56					
	IL	0.300 00	0.103 77						

^a IL for first design scenario: cation (2) 1-ethyl-3-methylimidazolium [emim], anion (1) dimethylphosphate [DMP]. IL for the second design scenario: cation (3) 1,3-dimethylimidazolium [dmim], anion (1) dimethylphosphate [DMP]. Global optimal results were obtained using the BARON⁵⁸ solver available in GAMS.⁵⁷ Operation pressure = 101.32 kPa. Flow of vapor = 0.28 mol. Flow of liquid = 0.72 mol.

Table 9. Second Potential IL Candidate for Ethanol Recovery^a

IL selected		compound	composition				some characteristics of selected IL			
			equilibrium			ratio of IL in operation temperature (K)	melting temperature (K)	boiling temperature (K)	molecular weight	solver used
			feed wt fraction	liquid	vapor					
				mole fraction	mole fraction					
cation (3) 1,3-dimethylimidazolium [dmim]	ethanol	0.749 70	0.759 61	0.920 39	20	352.8	322	426.6	184	SBB
anion (3) BF ₄ tetrafluoroborate	water	0.051 74	0.166 25	0.079 61						
	IL	0.198 56	0.074 13							
cation (3) 1,3-dimethylimidazolium [dmim]	ethanol	0.654 81	0.711 54	0.936 27	30	353.9	321.9	426.6	183.9	SBB
anion (3) BF ₄ tetrafluoroborate	water	0.045 19	0.165 04	0.063 73						
	IL	0.300 00	0.123 42							

^a Operation pressure = 101.32 kPa. Flow of vapor = 0.28 mol. Flow of liquid = 0.72 mol.

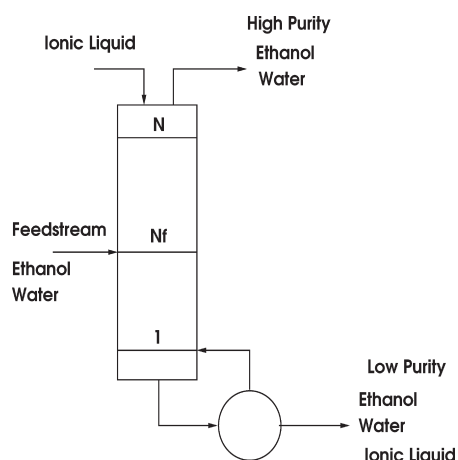


Figure 4. Flowsheet of the reboiled absorption column used for high-purity ethanol recovery from an azeotropic ethanol/water mixture using an optimally molecular designed IL as the solvent.

Finally, in Table 11, the detailed steady-state behavior of the flows, temperature, and composition profiles is provided for a 13-stage reboiled absorption column capable of performing the high-purity ethanol separation. In this last case, the ethanol/water mixture was fed on tray 5. Moreover, to make the process

profitable, the amount of recovered ethanol should also be high. From the results shown in Table 11, the mole fraction of ethanol (90%) turns out to be high. Of course, to really make the process of ethanol recovery using ILs profitable, a problem formulation based on formal optimization techniques should be used. Finally, because we expect the IL and water to feature different boiling points, an evaporation system could be used for water evaporation and for recovery of the IL as the heavy product. The recovered IL can then be recycled to the separation unit. Of course, we assume that the separation of water and the IL would not be a major problem mainly because of the differences in their relative volatilities. In the present work, we do not put too much attention on the IL recovery step because our aim is to concentrate our efforts on getting an optimally designed IL. However, we are aware of the importance of this step, and it will be addressed in a future work about the optimal design of the separation unit.

6. CONCLUSIONS

In this work, we have proposed a MINLP optimization formulation for approaching the optimal design of a new kind of green solvents specifically tailored to tackle the ethanol/water separation. This separation task has acquired renewed interest because of the need to use renewable fuels as a way to mitigate the

Table 10. Results of the Simulation of an Extractive Process

IL selected	compound	product composition		ratio IL in the global feed (wt %)	temperature (K)	
		liquid mole fraction	vapor mole fraction		stage <i>n</i>	stage 1
3	ethanol	0.747 94	0.977 95	20	351.7	369.7
	water	0.190 53	0.022 05			
	IL	0.061 54				
5	ethanol	0.741 00	0.995 79	20	352.5	369.3
	water	0.197 47	0.004 21			
	IL	0.061 54				
9	ethanol	0.739 51	0.999 62	20	355.3	369.3
	water	0.198 96	0.000 38			
	IL	0.061 54				

Table 11. Simulation Results with 13 Liquid–Vapor Equilibrium Stages (20% IL and 90% Ethanol Mole Fraction)

feed	stage	<i>T</i>	<i>F</i> ^L	<i>F</i> ^V	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>y</i> ₁	<i>y</i> ₂
0.9557	1	401.2	0.2684	0.0504	0.30244	0.53251	0.16505	0.67439	0.32561
	2	394.9	0.3189	0.1131	0.36129	0.49978	0.13894	0.73020	0.26980
	3	388.6	0.3815	0.1957	0.42923	0.45464	0.11613	0.78304	0.21696
	4	382.3	0.4642	0.3136	0.50511	0.39944	0.09545	0.83054	0.16946
	5	376.0	0.5821	0.4994	0.58699	0.33690	0.07612	0.87152	0.12848
	6	369.7	0.7678	0.8409	0.67257	0.26973	0.05770	0.90583	0.09417
	7	363.4	1.1094	2.5448	0.75983	0.20024	0.03994	0.93390	0.06610
	8	357.1	1.8575	2.7123	0.88582	0.09033	0.02385	0.97118	0.02882
	9	356.0	2.0250	3.0705	0.93972	0.03840	0.02188	0.98827	0.01173
	10	354.9	2.3833	3.7515	0.96647	0.01494	0.01859	0.99537	0.00463
	11	353.8	3.0643	5.3082	0.98001	0.00553	0.01446	0.99816	0.00184
	12	352.7	4.6210	17.8026	0.98839	0.00202	0.00959	0.99921	0.00079
0.0443	13	351.6	17.1154	0.7316	0.99661	0.00080	0.00259	0.99944	0.00056

effects of greenhouse gases on the environment. Traditionally, during the production of ethanol, the most expensive operation step is undoubtedly the separation task. Because of the presence of an azeotropic point, the ethanol/water separation has been carried out using nonsustainable solvents. One of our aims in this work was to demonstrate that this separation problem can be performed using a new generation of green solvents that can be synthesized to embed sustainable characteristics such as a low toxic level and a low vapor pressure, which means that they could be recovered and recycled.

Within the MINLP framework developed in this work, the molecular design of the IL is optimized such that it displays the greatest ethanol recovery with respect to the superstructure depicted in Figure 2. The model also considers the mole balances and the equilibrium relations using the UNIFAC method reported by Lei et al.³³ to determine the activity coefficients. Process restrictions and an objective function to maximize the ethanol purity of the product are considered also. The family of cations and anions used in the superstructure were obtained by analyzing the chemical stability, thermal stability, viscosity, melting point temperature, and water solubility of the possible ILs to be used. To verify that the optimum selected IL leads to the separation of the ethanol/water mixture up to the desired purity, simulations were done in a reboiled absorption column.

The MINLP model presented in this work can be extended to include new cations and anions to break or bypass the ethanol/

water azeotrope. Using improved property estimation, activity coefficient, and fugacity coefficient methods to address the vapor–liquid equilibrium are other possibilities. The objective function considered in the MINLP model maximizes the ethanol purity to a specified value. However, as can be seen in the results of the optimization and the simulations, as the ethanol purity increases, there is greater energy consumption (measured in terms of the increment in the temperature profile in the system). For a more realistic design scenario, it is clear that one needs to address the optimal design of the processing equipment where the separation task will take place. Furthermore, the interactions between the optimal design of the IL and the process should be exploited.

Finally, although by using the proposed MINLP formulation we were able to optimally design an IL to perform the ethanol/water separation under atmospheric conditions, it is clear that at least two routes could be used to check that the designed IL could realize such a separation. On the one hand, molecular simulation techniques could be used to verify the advantages of the IL in carrying out the aforementioned separation and to check some of the IL physical property values. On the other hand, the IL should be synthesized in the laboratory to fully demonstrate the separation characteristics. We think that the use of optimization formulations, like the one proposed in this work, is a powerful and effective way to speed up the discovery of new products featuring sustainable characteristics.

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NOMENCLATURE

Indexes

i (components) = CH₃OH, H₂O, IL (ionic liquid)
 j, k, m, n (functional groups for UNIFAC) = CH₃, CH₂, OH, H₂O, [mim][DMP], [im][DMP], [mim][CH₃SO₄], [im][CH₃SO₄], [mim][BF₄], [im][BF₄], [mim][Cl], [im][Cl], [mim][CF₃SO₃], [im][CF₃SO₃]

Variables

a_{nm} = UNIFAC group interaction parameter between groups n and m
 A_H = coefficient in the model equation for the melting temperature
 B_H = coefficient in the model equation for the melting temperature
 C_H = coefficient in the model equation for the melting temperature
 D_H = coefficient in the model equation for the melting temperature
 f = objective function
 F = molar flow of feed to the equilibrium stage
 F_i = auxiliary property for component i (surface fraction/mole fraction)
 $G_{m,n}$ = variable that considered the number of CH₃ and CH₂ groups ($n = 1, 2$) in the cation structure ($m = 1, 2, \dots, 5$)
 L = molar liquid flow from the equilibrium stage
 MW_i = molecular weight of component i
 MW_m^a = molecular weight of the anion m
 MW_m^c = molecular weight of the cation m
 n_m^{IL} = vector that contains the type and number of groups m of the IL selected
 P = pressure of the equilibrium stage (kPa)
 P_i° = vapor pressure of component i (kPa); t in °C
 q_i = parameter relative to the molecular van der Waals surface areas of pure component i
 Q_k, Q_m, Q_i = group surface area parameters in the UNIFAC model
 r_i = parameter relative to the molecular van der Waals volumes of pure component i
 R_k = group volume parameter in the UNIFAC model
 T = temperature of the equilibrium stage (K)
 $T_{\text{eb}}^{\text{H}_2\text{O}}$ = normal boiling temperature of water
 $T_{\text{eb}}^{\text{IL}}$ = normal boiling temperature of the molecular design IL
 ΔT_{eb} = temperature approach between the normal boiling temperature of water and the normal boiling temperature of the selected IL
 $T_{\text{mp}}^{\text{IL}}$ = melting temperature of selected IL (K)
 ΔT_{mp} = temperature approach between the temperature of the equilibrium stage and the melting temperature of the

selected IL

V = molar vapor flow from the equilibrium stage

V_i = auxiliary property for component i (volume fraction/mole fraction)

x_i = liquid mole fraction of component i in an equilibrium stage

X_m, X_n = fractions of group m in the mixture

y_i = vapor mole fraction of component i in an equilibrium stage

z_i = liquid mole fraction of component i in the feed equilibrium stage

z_{i-w} = weight fraction of component i in the feed equilibrium stage

Z_H = coefficient in the model equation for the melting temperature

Greek Variables

γ_i = activity coefficient of component i

γ_i^C = combinatorial contribution to the activity coefficient of component i

γ_i^R = residual contribution to the activity coefficient of component i

Γ_k = residual activity coefficient of group k

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecules of type i

δ = number of C substitutional groups in the molecule

θ_m, θ_n = fraction of group m or n in a mixture of the liquid phase

$\nu_k^{(i)}, \nu_m^{(i)}$ = number of groups of type k or m in molecule i

ψ_{nm}, ψ_{mk} = group interaction parameters

σ = number of the same groups that connect to >NH and =N— (ring of imidazolium)

τ = number of ring groups in the molecule

$\Omega_{k,n}$ = group interaction parameters

Ω_m^{OIL} = interaction parameters between the groups ($m = 1, 2, 3, 4$) and the molecular design of the IL

$\Omega_j^{\text{ILCH}_3}$ = interaction parameters between the IL ionic part ($j = 5, 6, \dots, 14$) and the CH₃ group

$\Omega_j^{\text{ILCH}_2}$ = interaction parameters between the IL ionic part ($j = 5, 6, \dots, 14$) and the CH₂ group

Ω_j^{ILOH} = interaction parameters between the IL ionic part ($j = 5, 6, \dots, 14$) and the OH group

$\Omega_j^{\text{ILH}_2\text{O}}$ = interaction parameters between the IL ionic part ($j = 5, 6, \dots, 14$) and the H₂O group

$\Omega_j^{\text{CH}_3\text{IL}}$ = interaction parameters between the CH₃ group and the IL ionic part ($j = 5, 6, \dots, 14$)

$\Omega_j^{\text{CH}_2\text{IL}}$ = interaction parameters between the CH₂ group and the IL ionic part ($j = 5, 6, \dots, 14$)

Ω_j^{OHIL} = interaction parameters between the OH group and the IL ionic part ($j = 5, 6, \dots, 14$)

$\Omega_j^{\text{H}_2\text{OIL}}$ = interaction parameters between the H₂O group and the IL ionic part ($j = 5, 6, \dots, 14$)

Binary Variables

σ_m = binary variable representing each cation m considered in the superstructure ($m = 1, 2, \dots, 5$)

α_m = binary variable representing each anion m considered in the superstructure ($m = 1, 2, \dots, 5$)

λ_K = binary variable representing the combination k between cations and anions in the superstructure ($k = 5, 6, \dots, 14$)

Definitions

$[\text{PF}_6]^-$ = hexafluorophosphate

$[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ = bis(triflyl)amide $\{\text{Tf}_2\text{N}^-\}$

$[\text{BF}_4]^-$ = tetrafluoroborate

$[\text{CF}_3\text{SO}_3]^-$ = triflate $\{\text{TfO}^-\}$

$[\text{NO}_3]^-$ = nitrate
 Br^- = bromide
 Cl^- = chloride
 I^- = iodide

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