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A novel hybrid process design for efficient recovery of hydrophilic ionic liquids from dilute aqueous solutions

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Abstract

Ionic liquids (ILs) have received much attention in both academia and industries due to their superior performance in many applications. Efficient recovery/recycling of ILs from their dilute aqueous solutions is essential for the acceptance and implementation of many IL-based technologies by industry. In this work, a practical and cost-effective hybrid process design method that combines aqueous two-phase extraction, membrane separation, and distillation operating at their highest efficiencies is proposed for the recovery of hydrophilic ILs from dilute aqueous solutions. The application of this hybrid process design method is illustrated through case studies of recovering two hydrophilic ILs, n-butylpyridinium trifluoromethanesulfonate ([C₄Py][TfO]) (CAS number: 390423-43-5) and 1-butyl-3-methylimidazolium chloride ([C₄mlm][Cl]) (CAS number: 79917-90-1), from their dilute aqueous solutions. For the recovery of 10 wt.% [C₄Py][TfO] from aqueous solution, the hybrid process using (NH₄)₂SO₄ as the salting-out agent could reduce the total annual cost (TAC) and energy consumption by 57% and 91%, respectively, compared with the pure distillation processes. In the case of recovering 10 wt.% [C₄mlm][Cl] from aqueous solution, the reduction in TAC and energy savings of the hybrid process with salting-out agent $(NH_4)_2SO_3$ could reach 49% and 87%, respectively, compared with the pure distillation process. Furthermore, uncertainty analysis through Monte Carlo simulations show that the proposed hybrid process design is more robust to uncertainties in energy prices and other material (e.g., equipment and solvent) costs.

KEYWORDS

aqueous two-phase extraction, hybrid process design, ionic liquid aqueous solution, ionic liquid recovery

1 | INTRODUCTION

Ionic liquids (ILs) as innovative fluids have been widely studied in different fields as many of them have very attractive properties including negligible vapor pressure, good thermal and chemical stability, and excellent catalysis performance. Some ILs also exhibit good solubility and selectivity for different gases as well as many organic and inorganic chemicals.¹ Besides these, ILs with desired properties can be

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. © 2023 The Authors. AIChE Journal published by Wiley Periodicals LLC on behalf of American Institute of Chemical Engineers. easily tailored for specific applications through tuning their molecular structures.¹ To date, different ILs have been used as absorbents in gas separations,^{2,3} extractants in liquid-liquid separation,^{4,5} catalysts in biomass conversion,^{6,7} electrolytes in batteries,^{8,9} and so on. However, most ILs are expensive, and they may have severe health related hazards and need to be carefully used and must be totally removed from any wastewater. For example, a well-known hydrophilic IL, 1-butyl-3-methylimidazolium chloride ($[C_4mIm][CI]$), was reported has severe health related hazards.¹⁰ Both economic and environmental concerns of applying ILs can be offset to some extent if they can be recycled/recovered efficiently. Therefore, efficient recycling/recovery of these high-value chemicals is essential for the acceptance and implementation of IL-assisted technologies by industry. So far, different separation approaches including extraction.¹¹ distillation.¹² membrane separation.¹³ adsorption.¹⁴ aqueous two-phase extraction (ATPE),¹⁵ electrodialysis,¹⁶ crystallization,¹⁷ and external force field separation¹⁸ have been introduced to recover/recycle ILs in different situations. All these separation approaches have their own advantages and disadvantages.¹⁹ For example, membrane separation is a robust and energyefficient way to recover ILs, but its feasibility is related to the flux, which largely limits its application in industry when large amounts of permeate needs to be handled. Currently, distillation and extraction are two of the most popular used separation methods for the IL recovery in both labs and industries.²⁰

As ILs generally have negligible vapor pressure, conventional distillation process is considered as the simplest operation for the recovery of ILs from volatile components. The volatile compounds can be removed by distillation, vacuum evaporation, and molecular distillation. In an IL-based process of the chlorination of butanediol (developed by BASF), the IL solvent is recycled by distilling water (formed as by-product) for the next run without any further processing.²¹ In the separation of methanol-trimethylborate mixtures using 1-ethyl-3-methylimidazolium tosylate ([C₂mim][TOS]) as entrainer, the recovery of IL is carried out by removing residual methanol in a falling film evaporator, and the recycled [C2mim][TOS] showed stable performance for this azeotropic separation during a period of 3 months.²² Huang et al.,²³ applied molecular distillation to recover [Amim] [CI] from aqueous solution of homogenous cellulose acetylation reaction media, where the volatile impurities are distilled and the recycled [Amim][Cl] is reused five times in this cellulose acetylation process without any change in IL-structure. On the other hand, extraction is an efficient method that is usually preferred in the recovery of ILs from nonvolatile and/or thermally sensitive substances. Generally, the hydrophobic ILs can be easily recovered from hydrophilic solutes through extraction with water. Ghatta et al. studied the synthesis of 5-hydroxymethylfurfural (5-HMF) from sugars in methyltrioctylammonium chloride, and this hydrophobic IL media is recycled from extracting 5-HMF with water.²⁴ In the case of recycling IL from solutes exhibiting immiscibility with water, organic solvents are generally used. For example, in a commercialized Sonogashira coupling reaction using tetraalkylphosphonium-based IL as the solvent, the Central Glass Company (Japan) use an organic solvent (hexane) to extract the

product, and the remaining IL-catalyst solution are reused several times with very limited loss of the catalytic activity.²⁵ However, the safety, health, environmental issues may come up with the introduction of the organic solvent.

In the case of recovering ILs from their dilute aqueous solutions, extraction methods typically require large solvent inputs to achieve high IL recovery, while distillation methods are extremely thermally inefficient due to the large amount of water needed to evaporate. For example, many studies reveal that some ILs have excellent performance in biomass pretreatment operations. However, large amounts of dilute aqueous solutions containing ILs are produced during this process.^{26,27} The disposal of these aqueous solutions will inevitably cause the loss of these high-value chemicals, and some of disposed ILs may even result in severe safety, health, environment issues. On the other hand, ATPE that is based on the formation of aqueous biphasic systems (ABS) is an efficient separation method in such cases since most ILs are concentrated in one phase by adding a small amount of salting-out agent.²⁰ Inorganic salts are the most common salting-out agents that have been used to induce the phase split of IL aqueous solutions, including potassium salts (K₂CO₃, K₃PO₄, and K₂HPO₄),²⁸ sodium salts (NaCl, Na₃PO₄, Na₂SO₄, Na₂CO₃, NaH₂PO₄),²⁹ and aluminum salts (Al₂(SO₄)₃, AlK(SO₄)₁₂H₂O).³⁰ Besides inorganic salts, some more benign species such as organic salts, carbohydrates and amino acids^{31,32} are also being studied as salting-out agents to induce phase split in the recovery of ILs from aqueous solutions.

In ABS, most ILs can be recovered from their dilute aqueous solutions when suitable salting-out agents are introduced, however, the IL-rich phase generally cannot meet the final purity requirement. Meanwhile, the energy consumption would be very high if ILs are recovered directly from distilling a large amount of water, even though distillation is a simple and efficient method to process aqueous solution with high IL concentration. Besides these, using membrane to concentrate IL aqueous solutions is much more difficult than salt aqueous solutions, and the membrane-based salt-water separation technologies have been widely used in industry. As reported, hybrid process schemes that combine two (or more) units operating at their highest process efficiencies to perform one (or more) process tasks are considered as potentially innovative and sustainable processing options.^{33,34} In this work, a hybrid process that combines ATPE, membrane separation, and distillation operating at their highest efficiencies are applied to recover ILs from dilute aqueous solutions. Although such a hybrid process has significant energy-saving potential, some challenges needed to be addressed for achieving the full potential of the process. For example, as both the structure of ILs and salting-out agents have significant impact on the formation of IL-ABS, it would be challenging to find high-performance salting-out agent(s) for ATPE process. Another challenge is how many salting-out agents should be used for aqueous solutions with different IL concentrations. All these questions are answered through case studies of recovering two wellknown hydrophilic ILs 1-butyl-3-methylimidazolium chloride ([C4mIm] [CI]) and n-butylpyridinium trifluoromethanesulfonate ([C₄Py][TfO]) from their dilute aqueous solutions.

2 | METHODOLOGY

In this work, a three-stage methodology that integrates salting-out agent screening, process design-simulation, and process evaluation (see Figure 1) is proposed for hybrid process design targeting the cost-effective recovery of hydrophilic ILs from their dilute aqueous solutions. The first design stage aims to select suitable salting-out agents for a given IL aqueous solution. The selection method includes two options: (1) salting-out agent(s) with high phase splitting ability for the given IL aqueous solution are selected from a comprehensive IL-ABS database and (2) a large number of potential salting-out agent candidates are generated through manipulating properties at the molecular level using computer-aided design technique and highperformance salting-out agent(s) are identified by solving an optimization-based mixed-integer nonlinear programming (MINLP) problem. A machine learning model that was proposed in previous work³⁵ is employed to describe the binodal curve behaviors of generated IL-ABS. It is essential to highlight that in order to guarantee the salting-out agent's compliance with the desired criteria and performance requirements, iterations involving the modification of design constraints and objectives are implemented in this design stage. The second stage involves process design and simulation for the recovery of ILs from dilute aqueous solutions. In this stage, hybrid separation scheme involving ATPE, distillation and reverse osmosis

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(RO) membrane separation is proposed. Afterwards, the process is rigorously simulated in Aspen Plus, where ILs are defined as pseudo components by specifying their critical properties and pure properties, while the UNIFAC-IL model is used for the phase equilibrium calculations of IL-water system. In the third evaluation stage, the energy and economic performance of different hybrid process schemes are thoroughly evaluated, and then Monte Carlo simulations are carried out to study how the cost uncertainties affect economic performance of the proposed hybrid process design.

2.1 | Selection of salting-out agent (stage-1)

2.1.1 | Option-a

The performance of the proposed hybrid process is highly dependent on the formation of ABS in ATPE. The ability of a salting-out agent to induce phase split of a given IL aqueous solution can be quantified through the binodal curve of the formed aqueous biphasic system. This curve denotes the separation between the two immiscible phases, as shown in Figure 2. Clearly, the closer to the axis origin a binodal curve is, the greater is the ability of a salting-out agent to create biphasic systems. Therefore, it is possible to identify highperformance salting-out agents for a given IL aqueous solution when



FIGURE 1 Framework of the hybrid process design for cost-effective recovery of ionic liquids from dilute aqueous solutions.



FIGURE 2 Binodal curve of ionic liquid-based aqueous biphasic systems $(x_{lL}, x_{lL}^T, x_{lL}^B$ and x_s, x_s^T, x_s^B are the weight fractions of ionic liquid and salting-out agent in the feed, top phase, and bottom phase, respectively).

the system's binodal data are available. Most recently, a comprehensive database covering 17,449 experimental binodal data points of 171 IL-based aqueous biphasic systems has been established previously.³⁵ This database allows one to find one or more salting-out agents to induce phase split for an included IL aqueous solution. In addition, the binodal curve of IL-ABS can also be used to guide the design of ATPS for the recovery of ILs form their dilute aqueous solutions. As the example presented in Figure 2 shows, the weight fraction of IL-rich phase will decrease when more salting-out agents are added to the system, which means that less solution (top phase) needs to be processed in further purification operations, but at the same time more IL remains in the bottom phase. All these changes can be easily quantified from the binodal curve, which is very important in the design of ATPS extraction process.

2.1.2 | Option-b

Selecting suitable salting-out agents from database is a reliable way, but it is severely limited by the available experimental binodal data. On the other hand, the optimal design of compounds/systems through manipulating properties at the molecular level is often the key to considerable scientific advances and improved process systems performance.³⁶ In this respect, an optimal ABS design method that was developed in previous work³⁷ provides the possibility of tailoring high-performance salting-out agents at the molecular level. This design method combines the computer-aided design technique and a machine learning model that is able to describe the binodal curve behaviors of IL-ABS. Similar to the design of many other compounds/ systems, a mathematical descriptor that can provide quantitative

information of IL-ABS is also needed for the optimal design of saltingout agents. As salting-out agents with different anions or cations generally present different phase splitting ability for different IL aqueous solutions, group contribution (GC) methods can be applied to describe the structure of the involved components in this salting-out selection (design) method. In this work, all potential salting-out selection (design) method. In this work, all potential salting-out agent candidates can be systematically generated from cation, anion, and molecule groups given in Table S1 (see supplementary material). High-performance salting-out agent(s) can be rapidly and reliably determined by solving an optimization-based MINLP problem that subjects to a series of design constraints, as described by Equation (3). Detailed information of MINLP problem for salting-out agent design can be found in Table S2 and the parameters of the machine learningbased predictive model is given in Table S4.

$$\begin{array}{ll} \max_{z,y} & \textit{TLL} \cdot (-S_{\textit{TL}})^r = f \big(z,y,\textit{T}^{as},\textit{H}^{lL},\textit{G}^{as} \big) \\ s.t. & \text{salting} - \text{out agent structural constraints} \\ & \text{mass balance constraints} \\ & \text{phase equilibria constraints} \end{array} \tag{1}$$

where *TLL* is the tie-line length (see Equation (2)) and S_{TL} is the slope of the tie-line (see Equation (3)); *r* is an adjustable parameter describing the degree of influence from *TLL* and S_{TL} . The value of *r* should be positive because, when IL-ABS has larger absolute values of S_{TL} (with a certain value of *TLL*), they require less salting-out agent inputs. Therefore, maximizing the objective function (in Equation ((1)) with positive values of *r* will yield better solutions. Continuous variable *z* denotes the ratio of added salting-out agent to the original IL aqueous solution, while discrete variables y represent the structure of generated salting-out agents. T^{as} is the system's temperature and G^{as} is the weight fraction of IL in the original IL aqueous solution. The structure of the specific IL molecule is described by vector H^{IL} . x_{IL}^T , x_{IL}^B and x_S^T , x_S^B , respectively, denote the weight fractions of ionic liquid and saltingout agent in the top phase and bottom phase, as shown in Figure 2.

$$TLL = \sqrt{\left(x_{S}^{T} - x_{S}^{B}\right)^{2} + \left(x_{IL}^{T} - x_{IL}^{B}\right)^{2}}$$
(2)

$$S_{TL} = \frac{x_{IL}^T - x_{IL}^B}{x_{S}^T - x_{S}^B}$$
(3)

The formulated MINLP problem is solved by a deterministic global optimization solver LINDOGLOBAL in the modeling system GAMS. This solver is based on the branch-and-bound algorithm and uses a rigorous bound tightening procedure to compute tight bounds on the feasible region of the MINLP problem. These help to reduce the search space and improve the efficiency of the solver. The solver also employs several cutting plane techniques and heuristics to accelerate the convergence to the global optimum. Given the limitations of the ANN-GC model in accurately predicting binodal curves near the axes, it may be necessary to adjust the composition of the generated IL-ABS in certain cases to enhance the reliability of the results.

2.2 | Hybrid process design and simulation (stage-2)

Different processing units have their own regions of efficient operations, the main concept of a hybrid process design is to ensure all involved units are operating at their high efficiency regions. In this work, the proposed hybrid process aims to combine ATPE, membrane separation, and distillation operating at their highest efficiencies in the recovery of ILs from dilute aqueous solutions. As shown in Figure 3, an aqueous biphasic system can be created through adding a certain amount of salting-out agent (determined in Section 2.1) to the dilute IL aqueous solution, and most IL is concentrated in the top phase. Then, the concentrated IL aqueous solution is sent to the distillation column, where pure IL can be obtained by distilling the rest of water. On the other hand, the salting-out agent aqueous solution is sent to a RO membrane unit, where most of the water is removed. Together with make-up agent, the remaining water and salting-out agent is recycled back to the ATPE unit. In this hybrid process, the RO membrane operates at high pressures to concentrate the salting-out agent aqueous solution as much as possible. As a result, the spiral-wound configuration is used because it offers high pressure resistance, high packing density, high recovery rates, and ease of maintenance.

Process simulation is a good option to use following the design or redesign of a process to check for feasibility and to analyze the efficiency of the process prior to implementation. In this hybrid process design, the process is rigorously simulated (Aspen Plus is used), and the equipment sizes and key operating variables are identified through a series of unit model calculations or sensitivity analysis. It is important to note that many ILs have specific thermal decomposition temperatures. Therefore, to prevent thermal decomposition, the maximum operating temperature of the distillation column should be lower than the IL's thermal decomposition temperature. This can be achieved by adjusting the column's operating pressure. As ILs are not included in the database of Aspen Plus, they are defined as pseudo-components by specifying the critical properties that can be obtained from a fragment contribution-corresponding states method.³⁸ In this work, Aspen Plus uses the UNIFAC-IL model³⁹ as a thermodynamic tool to predict the VLE behavior of IL-water system based on the molecular structure and composition of the components, and the corresponding interaction parameters. Meanwhile, Aspen Plus considers separation kinetics in the sizing of distillation columns by

using rigorous tray models to estimate the mass transfer rate and tray efficiency, which are used to determine the number of trays required for a given separation task, and optimize the design of the column for maximum separation efficiency. In addition, a sensitivity analysis is performed to identify and optimize the key factors that influence the performance of the process.

In this work, the process simulation is performed under the following assumptions: (1) the process is operating under steady-state conditions, meaning that the process variables are constant over time; (2) the physical properties of the materials used in the process are constant over time; (3) the mixtures in the process are homogeneous, meaning that the composition is the same throughout the mixture; and (4) mixing is ideal, meaning that the components in the mixture are evenly distributed. It is important to note that these assumptions are not always accurate for real-world processes, and the accuracy of Aspen simulation results depends on the validity of these assumptions. Therefore, it is crucial to further validate the simulation results with experimental data and adjust the model as necessary to ensure its accuracy.

2.3 | Process evaluation (stage-3)

Process evaluation a critical step that attempts to analyze and examine the effectiveness and efficiency of a process. Energy consumption is a key indicator of any process evaluation, especially energy-intensive processes. Generally, the energy consumption of a separation process mostly comes from the input of thermal energy and electricity, and the total energy consumption (*TEC*) can be expressed by an equivalent electricity energy penalty by Equation (4).⁴⁰ In order to quantify the energy performance of a process, a specific energy consumption (*SEC*), as expressed by Equation (5), is introduced.

$$TEC = W_e + Q_{th}\eta \tag{4}$$

$$SEC = \frac{TEC}{m_{lL}}$$
(5)

where W_e is the electricity consumption in compressor and pump, Qth is the heat duty in the last flash, and η is the conversion efficiency of



FIGURE 3 Hybrid process scheme for the recovery of ionic liquids from dilute aqueous solutions.

thermal energy to electricity, which is estimated to be 0.3–0.4,⁴¹ and 0.384 is used in this work. m_{lL} is the mass flow of the recovered IL, the units of *TEC* and *SEC* are MJ/h, MJ/kg IL, respectively.

Apart from energy consumption evaluation, economic evaluation that aims to assess the cost effectiveness of a process is also playing an important role in the decision-making process. The purpose of economic evaluation is to identify the best course of action, based on the available data. An economic evaluation will measure two parameterscost and outcome. As given in Table S5, the total annual cost (TAC) of a process can be represented by the sum of the annualized capital cost (ACC) and total operating expense (OPEX). The ACC is calculated from the translation of the total capital expense (CAPEX) (see Equation 5), and the detailed calculations of $CAPEX^{42,43}$ are given in Table S6. The purchased equipment cost of distillation column and utility cost in OPEX are computed from Aspen Process Economic Analyzer (APEA). The equipment cost of flash tank for preliminary ILwater separation and pumps are evaluated based on models proposed by Couper et al.⁴⁴ All the equipment costs are updated to the year 2022 with the Chemical Engineering Cost Index.⁴⁵ For the membrane evaluation, the capital cost is scaled up according to the water treatment, in which 3\$/kg per hour water treatment.⁴⁶ Detailed calculation methods can be found in Table S6.

$$ACC = \frac{CAPEX}{\left(\left(1+ir\right)^{n}-1\right)/ir\left(1+ir\right)^{n}}$$
(5)

where *ir* and *n*, respectively, denote the annual interest rate (8%) and the project lifetime (25 years).⁴⁷

On the other hand, the OPEX has two parts: one is the variable operating cost (VOC) which includes the salting-out agent input/ make-up and the public utilities such as heat steam, cooling water and electricity. The other part is the fixed operating cost (FOC) that contains the maintenance, operating labor, etc. Detailed calculation methods are presented in Table S7.43 In the calculation of operating cost, the following costs are considered for different types of utilities: 0.08\$/kWh electricity; 0.0329\$/ton cooling water; 24.7\$, 31\$, and 37.2^{\$}/ton steam of low, medium, and high pressure, respectively. To calculate cost of the solvent make-up, the price of different salts is estimated to be 340\$/ton (NH₄)₂SO₄, 1450\$/ton K₃PO₄, 900\$/ton KH₂PO₄, 350\$/ton (NH₄)₂SO₃ under the industrial production. In industry, the operating cost of a membrane separation process is generally calculated based on the amount of water treatment, and the operating cost of salt-water membrane separation is much easier than that of IL-water membrane separation. In this work, the operating cost of membrane separation for salt-water and IL-water are assumed to be 11.2\$/ton water and 8.4\$/ton water, respectively. The membrane operating cost and the prices of electricity, utilities and solvents are obtained from market inquiry and personal communication with engineers in industry.

Uncertainty analysis aims to make a technical contribution to decision-making through the quantification of uncertainties in the relevant variables. It has been widely reported that the Monte Carlo Method offer many advantages over conventional approaches in the uncertainty studies, particularly those involving complex measurement systems' outputs.⁴⁸ In this hybrid process design, Monte Carlo simulations are performed to quantify the variability of the economic performance (TAC) with the uncertainties in energy prices (e.g., electricity and steam), capital investment and other costs such as working capital and solvent cost. Generally, energy prices are more sensitive than other inputs within a time period, for example, price changes in 2022. For this reason, energy prices with an uncertainty of ±30% is used in Monte Carlo simulations, and for other costs an uncertainty of ±20% is set. In this work, Monte Carlo simulations are carried out in Jupyter Notebook, a web-based interactive computing platform.

3 | CASE STUDIES

1-Butyl-3-methylimidazolium chloride ([C4mIm][Cl]) is a highly efficient direct IL-solvent for the dissolution and regeneration of cellulose and large volumes of dilute IL aqueous solutions are produced during the precipitation of the regenerated cellulose.^{26,27} As reported, this hydrophilic IL has severe health related hazards.¹⁰ Therefore, efficient recycling of [C₄mIm][Cl] from these aqueous solutions is a critical step for the commercialization of this IL-based pretreatment technology. *n*-Butylpyridinium trifluoromethanesulfonate ([C₄Py][TfO]) is another well-known hydrophilic IL that has potential industrial applications. Safety related properties have not been studied for this IL, but it is also important to recover it from aqueous solutions during application. In this section, the proposed hybrid process design method is applied to the recovery of [C₄mlm][Cl] and [C₄Py][TfO] from dilute aqueous solutions and a representative concentration of 10 wt.% IL is studied. Separation processes using only distillation or nanofiltration (NF)¹³distillation (a hybrid process combines NF membrane separation and distillation technologies) are also studied. In each case, four different processes (including two hybrid processes with different salting-out agents) are compared under the same IL purity requirement (>99.5%). The parameters used for property predictions and process simulations (in Aspen Plus) are given in Tables S8-S10. Phase diagrams for the [C₄Py][TfO]-water and [C₄mlm][Cl]-water systems are provided in Figures S1 and S2, respectively. The equipment designs of ATPE unit, distillation column and membrane unit are provided in Tables S12-S14.

4 | RESULTS AND DISCUSSION

4.1 | Case 1–[C₄Py][TfO] recovery

4.1.1 | Selection of salting-out agents (stage-1)

To find a suitable salting-out agent that can induce the phase split of $[C_4Py][TfO]$ aqueous solution, this work first performs a data search against the IL-ABS database. All the experimental $[C_4Py][TfO]$ -involved ABSs are retrieved and then displayed in Figure 4. It is found that all reported experimental salting-out agents have very similar



FIGURE 4 Experimental binodal curves of [C4Py][TfO]-involved aqueous biphasic systems.^{50,51}

ability of inducing a phase split in the [C₄Py][TfO] aqueous solution. Nonetheless, ammonium sulfate ((NH₄)₂SO₄) at 298 K still shows a slightly better ABS formation performance than the others. When using computer-aided selection method, potassium dihydrogen phosphate (KH₂PO₄) was identified to have the best ABS creation ability for [C₄Py][TfO] aqueous solution. Model details from GAMS solution of the MINLP-based IL-ABS design problem are given in Table S8. The binodal curves of ABS formed by [C₄Py][TfO] $+ (NH_4)_2SO_4 + H_2O$ and $[C_4Py][TfO] + KH_2PO_4 + H_2O$ are shown in Figure 5. To achieve a more feasible IL-ABS, a (x_{11}^T, x_5^T) value of (0.494, 0.023) is applied for $[C_4Py][TfO] + KH_2PO_4 + H_2O$, instead of using a value of (0.880, 0.019) which was identified directly from model optimization. Obviously, compared with (NH₄)₂SO₄, less KH₂PO₄ input is needed to induce phase split in the [C₄Py][TfO] aqueous solution, but the highest reachable concentration of $[C_4 Py]$ [TfO] in $(NH_4)_2SO_4$ -based ABS is higher than that of KH_2PO_4 -based ABS. For an aqueous solution containing 10 wt.% [C₄Py][TfO], the phase formation information of ABS $[C_4Py][TfO] + (NH_4)_2SO_4 + H_2O_4$ and $[C_4Py][TfO] + KH_2PO_4 + H_2O$ is provided in Table 1.

4.1.2 | Process design and simulation (stage-2)

For the hybrid IL-water separation process, the key operation parameters including the agent input amount, distillate mass flow and reflux ratio are optimized. Taking $[C_4Py][TfO]$ -water separation as an example, a series of sensitivity analysis are performed and the results of this analysis are presented in Figures 5–7. Obviously, the reboiler heat duty in distillation column decreases significantly with increasing the input of (NH₄)₂SO₄. This is because when more salting out is added to the system, more water is transferred to the bottom phase, which means less water needs to be distilled in the distillation column. On the other hand, the purity of water (at column top) will increase first



 $\begin{array}{ll} \mbox{FIGURE 5} & \mbox{Experimental and calculated binodal curves of ABS} \\ \mbox{formed by } [C_4 Py][TfO] + (NH_4)_2 SO_4 + H_2 O^{50} \mbox{ and } [C_4 Py][TfO] \\ + \mbox{KH}_2 PO_4 + H_2 O \mbox{ (model parameters are given in Tables S3 and S4)}. \end{array}$

and then decrease with the increase of the salting-out agent input, and for the purity of IL (at column bottom) it will also increase first but then remain at a stable value, as shown in Figure S3. As expected, the reboiler heat duty in distillation column increases gradually when reflux ratio is increased. With such a change, the purity of both water and IL will increase first and then remain at stable values, as illustrated in Figure S4. The increase of distillate mass flow has similar impact on the purity of water and IL, as presented in Figure S5. The details of the equipment sizes and operation parameters are given in Tables S12–S14. As reported,⁴⁹ the thermal decomposition temperature of most ILs containing anion [TfO] is above 600 K. Since the maximum operating temperature of the process is about 400 K, and therefore no IL decomposition will happen in the whole process.

4.1.3 | Process evaluation (stage-3)

Different cost contributions to the total annual cost (TAC) of four separation processes targeting the recovery of 10% wt. $[C_4Py][TfO]$ from aqueous solution (10 t/h) are given in Table 2. In this case, the TAC of NF-distillation process is 2560k\$ and the TAC of distillation process is 3769k\$. For the hybrid processes with (NH₄)₂SO₄ and KH₂PO₄, the TACs are 1634k\$ and 2371k\$, respectively. To better illustrate the difference in economic performance of each process, Figure 6 that directly compares the TAC and every cost contribution of all studied separation processes is also provided. Obviously, the hybrid process using salting-out agent (NH₄)₂SO₄ or KH₂PO₄ has much better economic performance than the pure distillation and NF-distillation processes. The hybrid process with KH₂PO₄ could reduce TAC by 36% and 8%, respectively, compared with the pure distillation and NFdistillation processes. Remarkably, the reduction in TAC of using the hybrid process with (NH₄)₂SO₄ could even reach 57% and 37% **TABLE 1** ABS information of $[C_4 m lm][Cl] + K_3 PO_4/(NH_4)_2 SO_3 + H_2O$ and $[C_4 Py][TfO] + (NH_4)_2 SO_4/KH_2 PO_4 + H_2O$ for 10 wt.% IL aqueous solutions

Aqueous solution Salting out-agent	[C₄mlm][Cl] (10 wt.%)		[C ₄ Py][TfO] (10 wt.%)	
	K ₃ PO ₄	(NH ₄) ₂ SO ₃	(NH ₄) ₂ SO ₄	KH ₂ PO ₄
x _{IL}	0.384	0.508	0.699	0.494
x _S ^T	0.040	0.026	0.014	0.023
x _{H₂O}	0.576	0.466	0.287	0.483
x ^B _{IL}	0.021	0.005	0.017	0.003
x _S ^B	0.335	0.201	0.303	0.161
x ^B _{H2O}	0.644	0.794	0.680	0.836
x _{IL}	0.070	0.082	0.072	0.088
X _S	0.296	0.175	0.281	0.136
x _{H2O}	0.634	0.743	0.647	0.776
$M^T / (M^T + M^B)$	0.135	0.152	0.080	0.173
$M^{B}/(M^{T}+M^{B})$	0.865	0.848	0.920	0.827
TLL	0.468	0.533	0.740	0.509
S _{TL}	-1.232	-2.877	-2.360	-3.563

Note: M^{T} , mass of top phase, M^{B} , mass of bottom phase.



FIGURE 6 Total annual cost comparison for case I ([C₄Py][TfO]– water separation) of four different separation processes.

compared with the pure distillation and NF-distillation processes, respectively. Membrane operating cost and FOC contribute more than 50% of TAC in the hybrid process with KH_2PO_4 or $(NH_4)_2SO_4$, while Steam cost and FOC are the two major contributions to TAC in the pure distillation and NF-distillation processes. Due to the introduction of ATPE and membrane technologies, the energy-related cost of TAC in hybrid processes with $(NH_4)_2SO_4$ and KH_2PO_4 are, respectively, reduced by 91% and 80% compared with the pure distillation process. The specific energy consumption (SEC) of pure distillation processes with $(NH_4)_2SO_4$ and KH_2PO_4 and KH_2PO_4 and KH_2PO_4 and $(NH_4)_2SO_4$ and KH_2PO_4 and $(NH_4)_2SO_4$ and $(NH_4)_$

compared to the NF-distillation separation process, 81% and 58% energy savings are obtained by introducing ATPE technology to the hybrid processes with $(NH_4)_2SO_4$ and KH_2PO_4 , respectively.

Uncertainty analysis is performed to quantify the variability of the economic performance with the uncertainties in energy prices (\pm 30%) and other costs (\pm 20%). Figure 7 presents the total annual cost (TAC) range of four different processes based on 10,000 Monte Carlo simulations for the separation of [C₄Py][TfO]–water. The uncertainties in TAC are: \pm 403.33k\$ (25%) for the hybrid process with (NH₄)₂SO₄, \pm 504.68k\$ (21%) for the hybrid process with KH₂PO₄, \pm 724.95k\$ (28%) for the NF-distillation separation process, and \pm 1308.81k\$ (35%) for the pure distillation process. Obviously, the economic performance of hybrid processes with (NH₄)₂SO₄ and KH₂PO₄ are more robust than that of NF-distillation and distillation processes. These uncertainty study results demonstrate that the concept of a hybrid process design has similar advantages to a diversified portfolio in reducing the overall economic risk profile.

4.2 | Case 2–[C₄mIm][CI] recovery

4.2.1 | Selection of salting-out agents (stage-1)

For the case of $[C_4mlm][Cl]$ aqueous solution, the binodal curve data retrieved from IL-ABS database are illustrated in Figure 8. It is found that tripotassium phosphate (K₃PO₄) at 298 K presents the highest ABS formation ability for $[C_4mlm][Cl]$ aqueous solution. On the other hand, ammonium sulfite ((NH₄)2SO₃) was determined by computeraided design method to be the best salting-out agent for inducing the ABS formation of $[C_4mlm][Cl]$ aqueous solution. Figure 9 presents



Total annual cost

FIGURE 7 Total annual cost range of four different separation processes based on 10,000 Monte Carlo simulations for case I ($[C_4Py][TfO]$ -water separation).

TABLE 2 Cost contributions to total annual cost of different separation processes for the recovery of 10 wt.% $[C_4Py][TfO]$ from aqueous solution (10 t/h).

	Hybrid process with (NH ₄) ₂ SO ₄	Hybrid process with KH ₂ PO ₄	NF-distillation	Distillation
ACC (10 ³ \$/y)	6.27	8.41	21.69	37.05
FOC (10 ³ \$/y)	805.12	895.91	1218.16	1645.16
Steam cost (10 ³ \$/y)	126.79	341.34	858.36	1867.29
Cooling water cost (10 ³ \$/y)	6.68	17.95	65.32	142.32
Electrical cost (10 ³ \$/y)	40.77	38.62	40.72	35.87
Solvent make-up (10 ³ \$/y)	53.12	380.16	0.00	0.00
Membrane cost (10 ³ \$/y)	579.10	659.20	329.76	0.00
VOC-miscellaneous operating materials (10 ³ \$/y)	16.46	29.33	26.41	41.74

the binodal curves of ABS formed by $[C_4mIm][CI] + K_3PO_4 + H_2O$ and $[C_4mIm][CI] + (NH_4)_2SO_3 + H_2O$. Clearly, $(NH_4)_2SO_3$ has better phase splitting ability than that of K_3PO_4 in the aqueous solution of $[C_4mIm]$ [CI]. Obviously, ATPE using $(NH_4)_2SO_3$ has higher recovery efficiency and less salting-out agent input than ATPE using K_3PO_4 under the condition of no salting-out agent recycling. This means that less IL aqueous solution needs to be recycled to ATPE unit in the hybrid process with $(NH_4)_2SO_3$, leading to the equipment cost reduction and energy savings. The ABS formation information of $[C_4mIm][CI] + K_3PO_4 + H_2O$ and $[C_4mIm][CI] + (NH_4)_2SO_3 + H_2$ targeting the recovery of 10 wt.% $[C_4mIm][CI]$ from aqueous solution is also provided in Table 1.

4.2.2 | Process design and simulation (stage-2)

By applying the same process design and simulation strategy that used in Case 1, the equipment sizes and the key operation parameters including the agent input amount, distillate mass flow and reflux ratio are identified for this case, as summarized in Tables S12–S14. It is worth mentioning that the thermal decomposition temperature of is [C₄mIm][CI] about 520 K⁴⁹ and the maximum operating temperature of the process is lower than 470 K, which means that the IL can stay thermal stability through the whole process.



FIGURE 8 Experimental binodal curves of [C₄mlm][Cl]-involved aqueous biphasic systems.^{52–54}



FIGURE 9 Experimental and calculated binodal curves of ABS formed by $[C_4mlm][Cl] + K_3PO_4 + H_2O^{53}$ and $[C_4mlm][Cl] + (NH_4)_2SO_3 + H_2O$ (model parameters are given in Tables S3 and S4).

4.2.3 | Process evaluation (stage-3)

The cost contributions to TAC of all studied separation processes for the recovery of 10% wt. [C₄mim][Cl] from aqueous solution (10 t/h) are provided in Table 3. In this case, the TAC of NF-distillation process is 2859k\$ and the TAC of distillation process is 4677k\$. For the hybrid processes with K₃PO₄ and (NH₄)₂SO₃, the TACs are 2696k\$ and 2357k\$, respectively. Figure 10 is provided to have a better illustration of the difference in economic performance of each separation process in this case. Similar to the first case, the hybrid process using salting-out agent K₃PO₄ or (NH₄)₂SO₃ also outperform their counterparts, the pure distillation and NF- processes. Simulation and calculation results show that the hybrid process with K₃PO₄ could reduce TAC by 42% and 6%, respectively, compared with the pure distillation and NF- distillation processes. The hybrid process with (NH₄)₂SO₄ even gives a better economic performance, and the reduction in TAC could reach 49% and 18% compared with the pure distillation and NF- distillation processes, respectively. In addition to Membrane operating cost and FOC, Solvent make-up and Steam cost also make certain contributions to TAC in hybrid processes, especially for the hybrid process with K₃PO₄. On the other hand, Steam cost contributes more than 65% and 47% of TAC in the pure distillation and NFdistillation processes, respectively. In this case, the energy-related cost of TAC in hybrid processes with K₃PO₄ and (NH₄)₂SO₃ are, respectively, reduced by 83% and 87% compared with the pure distillation process. The SEC of pure distillation process is 11.52 MJ/kg [C₄mim][Cl] recovery, and for the hybrid processes with K₃PO₄ and (NH₄)₂SO₃ they are 2.01 and 1.44, respectively. When compared to the NF-distillation process, 61% and 72% energy reductions are achieved by using hybrid processes with K_3PO_4 and $(NH_4)_2SO_3$. respectively.

For the uncertainty study of $[C_4mim][CI]$ -water separation, Monte Carlo simulations are also performed to quantify the variability of TAC with the uncertainties in energy-related costs of ±30% and other costs of ±20%. The TAC range of four different processes based on 10,000 Monte Carlo simulations is illustrated in Figure 11. In this case, the uncertainties in TAC are: ±586.38k\$ (22%) for the hybrid process with K₃PO₄, ±513.31k\$ (22%) for the hybrid process with (NH₄)₂SO₃, ±921.62k\$ (32%) for the NF-distillation separation process, and ± 1921.35k\$ (41%) for the pure distillation process. Similar

TABLE 3 Cost contributions to total annual cost of different separation processes for the recovery of 10 wt.% [C₄mim][Cl] from aqueous solution.

	Hybrid process with K_3PO_4	Hybrid process with (NH ₄) ₂ SO ₃	NF-distillation	Distillation
ACC (10 ³ \$/y)	7.80	6.96	12.97	22.06
FOC (10 ³ \$/y)	899.27	861.40	1030.03	1342.77
Steam cost (10 ³ \$/y)	498.06	349.59	1356.07	3061.69
Cooling water cost (10 ³ \$/y)	24.23	16.72	55.85	142.33
Electrical cost (10 ³ \$/y)	41.00	38.62	39.42	34.75
Solvent make-up (10 ³ \$/y)	720.07	408.82	0.00	0.00
Membrane cost (10 ³ \$/y)	471.02	648.13	329.76	0.00
VOC-miscellaneous operating materials (10 ³ \$/y)	35.80	29.83	36.35	66.10

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to the case of $[C_4Py][TfO]$ -water separation, hybrid processes with $(NH_4)_2SO_4$ and KH_2PO_4 in the separation of $[C_4mim][CI]$ -water also have obviously higher robustness in economics than the NF-distillation separation process, especially the distillation process. These uncertainty study results suggest again that the concept of a hybrid process design would definitely lower the overall economic risk profile.



FIGURE 10 Total annual cost comparison for case II ([C₄mim] [CI]-water separation) of four different separation processes.

As illustrated above, the hybrid process with a salting-out agent selected from the database or identified by the computer-aided molecular design method presents better economic performance and higher robustness in economics than the NF-distillation process, especially the pure distillation process in both cases. On the other hand, the hybrid process using different salting-out agents will exhibit different economic performance, demonstrating the important effect of the phase splitting ability of a salting agent on the overall economic performance of the proposed hybrid process. In the first case, the hybrid process with salting-out agent $((NH_4)_2SO_4)$ identified from database screening demands lower TAC and less solvent make-up than that of the hybrid process with salting-out agent (KH₂PO₄) determined by the computer-aided molecular design method. On the contrary, in the second case, the hybrid process using (NH₄)₂SO₃ (tailored by the computer-aided design method) present better economic performance and less solvent make-up than the hybrid process using K₃PO₄ (selected from database). These results suggest that the salting-out agent screening approach that combines database screening and computer-aided design method would improve the chances of achieving the best performing hybrid process design.

In addition, the results obtained in this study demonstrate the sensitivity of the proposed hybrid process scheme to the selection of salting-out agents. To address the challenge of salting-out agent selection in a more systematic manner, we recommend implementing a screening or optimization approach specifically focused on saltingout agents. This approach could involve evaluating a wider range of



Total annual cost

FIGURE 11 Total annual cost range of four different separation processes based on 10,000 Monte Carlo simulations for case II ([C₄mim][CI]– water separation).

salting-out agents, exploring different concentrations or combinations, and conducting comprehensive experimental or computational studies to identify the most suitable options. Furthermore, considering the impact of process parameters such as temperature, pressure, and mixing conditions on the performance of salting-out agents could provide additional insights and contribute to the systematic resolution of this challenge.

5 | CONCLUSION

This work presents a three-stage hybrid process design method that aims to combine aqueous two-phase extraction (ATPE), membrane separation, and distillation operating at their highest efficiencies for the recovery of hydrophilic ILs from dilute aqueous solutions. In stage-1, high-performance salting-out agents are reliably and efficiently selected for ATPE through both database screening and computer-aided solvent design methods. In stage-2, the equipment sizes and operation parameters of the hybrid process are determined through model calculations (e.g., membrane area and ATPE area) or sensitivity analysis (e.g., reflux ratio, number of stages, and feed stage location) in rigorous process simulations. In stage-3, the energy and economic performance of the hybrid process is evaluated and the impact of cost uncertainties on the economic performance is studied through Monte Carlo simulations. Two case studies are performed to test the applicability and effectiveness of this hybrid design method. In the case of recovering 10 wt.% [C₄Py][TfO] from aqueous solution, the hybrid process with (NH₄)₂SO₄ and KH₂PO₄ could reduce the total annual cost (TAC) by 57% and 37%, respectively, compared with the pure distillation process. For the recovery of 10 wt.% [C₄mlm] [CI] from aqueous, the reduction in TAC of using the hybrid process, respectively, with K_3PO_4 and $(NH_4)_2SO_3$ could reach 42% and 49% compared with the pure distillation process. Due to the introduction of ATPE and membrane technologies, the energy-related cost of TAC in hybrid processes with (NH₄)₂SO₄ and (NH₄)₂SO₃ are, respectively, reduced by 91% and 87% compared with the pure distillation process. When compared to the NF-distillation process, 81% and 72% energy savings are achieved by introducing ATPE technology to the hybrid processes with (NH₄)₂SO₄ and (NH₄)₂SO₃, respectively. These results suggest that the concept of combining different technologies operating at their highest efficiencies has great potential for process design and intensification. Furthermore, Monte Carlo simulations indicate that the hybrid process design would also improve the economic robustness of the process, which is of great importance for the acceptance and implantation of this separation method in industry.

It is worth noting that the salting-out agent selection and process design problems are solved independently in the present work, and a more attractive global optimal solution might be attainable through simultaneous design. However, computational efficiency could be a limiting factor as the complexity and the design space of the globalbased MINLP problem will increase significantly. In this regard, more advanced MINLP solving algorithms as well as more powerful computers are highly desired. For the hybrid process design itself, the phase splitting ability of a salting agent in ATPE has an important influence on the process performance. Comparisons of different hybrid processes in two cases indicate that the salting-out agent selection approach that combines database screening and computeraided design method would improve the chances of achieving the best performing hybrid process design. In addition, there is a possibility that salting-out agents identified by the computer-aided design method may not work as expected due the uncertainties of the phase behavior predictive model. Therefore, it is crucial to further validate the results with experimental data and adjust the model as necessary to ensure its accuracy. Efficient recovery of ILs from dilute aqueous solutions is a critical step to make IL-based technologies costeffective and environmentally friendly. This work has the potential to make a significant impact on the commercialization of IL-based technologies in various fields, especially in the pretreatment of lignocellulosic biomass, which would undoubtedly boost the development of biorefineries. In addition, the hybrid design method proposed in this work could potentially be extended to other solvent recovery applications, such as wastewater treatment in the pharmaceutical industry.

AUTHOR CONTRIBUTIONS

Yuqiu Chen: Conceptualization (lead); investigation (lead); methodology (lead); software (equal); writing – original draft (lead). Xinyan Liu: Methodology (equal); software (equal); writing – review and editing (equal). Yang Lei: Writing – review and editing (equal). Xiaodong Liang: Project administration (equal); writing – review and editing (equal). Rafiqul Gani: Methodology (equal); writing – review and editing (equal). Georgios M. Kontogeorgis: Funding acquisition (lead); supervision (lead); writing – review and editing (equal).

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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