Assessment of bio-ionic liquids as promising solvents in industrial separation processes: Computational screening using COSMO-RS method

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A R T I C L E   I N F O

A B S T R A C T

The use of organic solvents in the chemical industry for gas-liquid absorption or liquid-liquid extraction operations is still unavoidable. The search of "greener" solvents to replace fossil-based counterparts is a challenge for the scientific community. Biocompatible ionic liquids (bio-ILs) emerged as a sustainable approach for the development of greener processes. In this work, bio-ILs based on choline as common cation are evaluated as promising solvents in typical industrial separation processes such as gas absorption (refrigerants, CO_2, H_2S, NH_3, or acetone) and liquid-liquid extraction (hydrocarbon separations, denitrogenation, desulfurization, and recovery of value-added compounds and/or contaminants from aqueous streams) by means of COSMO-RS method. Some bio-ILs show competitive behavior compared to the benchmark common ILs solvents for all the solutes evaluated. None of the solvents evaluated is predicted to form two liquid phases in aqueous solutions, so future work should be conducted on finding hydrophobic bio-ILs to perform these separations. On the other hand, bio-ILs in hydrocarbon separations by means of liquid-liquid extraction show competitive results in terms of selectivities (benzoate-based) and partition coefficients (bicarbonate-based) compared to benchmark sulfolane and common ILs previously tested.

1. Introduction

Nowadays, large quantities of organic solvents are needed for different separation processes in the chemical industry such as gas-liquid absorption or liquid-liquid extraction operations [1]. The annual industrial production of organic solvents is almost 20 million of metric tons [2]. The excessive consumption of toxic solvents is also known as typical example of unsustainable practices. However, the use of solvents is still unavoidable in many processes, so different alternative chemical procedures have been proposed to reduce the amount of toxic, or harmful organic solvents, enhancing the sustainability of the processes [2]. In the last years, different families of "green solvents" have been proposed to replace fossil-based counterparts, such as bio-ionic liquids, bio deep eutectic solvents, liquid polymers, or solvents synthetized from CO_2 [2].

In the last decades, global temperature has been increasing every year, principally caused by the presence of atmospheric greenhouse gasses (GHGs) in high concentrations [3]. Paris agreement in 2015 limited the global temperature increase between 1.5 °C and 2 °C above pre-industrial levels [4]. Global GHG emissions are attributed to different sectors such as energy systems, industry, buildings, and transport [5]. Carbon dioxide (CO_2) accounts for at least 2/3 of global GHG emissions. However, other gasses such as methane (CH_4), nitrous oxide (N_2O) or industrial gasses such as hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), volatile organic compounds (VOCs) or nitrogen trifluoride (NF_3) are also contributing to global warming [6]. Intergovernmental Panel on Climate Change (IPCC) report shows that about 79% of the total CO_2 emissions come from fossil fuels used for power generation [7]. Therefore, the removal of CO_2 from flue-gasses produced in power plants is a solution widely adopted to reduce the carbon emissions in the energy and chemical sectors [8]. Depending on the place where the CO_2 capture unit is located in the chemical plant, the process can be divided into pre-combustion, oxy-combustion, or post-combustion. Different technologies have been developed for CO_2 removal including, physi-

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cal and chemical absorption, adsorption, membranes, or cryogenics [8]. The most extended solution is the chemical absorption with aqueous amines: monoethanolamine, or methyl diethanolamine, among others. However, it presents some disadvantages in its use principally caused by their high volatility and corrosion [8]. On the other hand, despite being limited in the Kigali Amendment to the Montreal Protocol, in 2020 HFC consumption in the EU+UK increased by 7% compared with 2019 [9]. Global emissions have also increased in the last years, being estimated that in 2018 HFC-23 emissions were higher than any previous value recorded [10]. Besides, HFCs global warming potential is very high (reported values of 23,000 times higher than that of CO_2 [11]) so the environmental impact associated with HFC emissions cannot be neglected. On the contrary, they possess interesting transport and thermodynamic properties for cooling applications, being widely used as refrigerants in both domestic and industrial systems (including absorption refrigeration cycles) [12]. Among them, R-32, R-125 and R-134a stand out as the most extensively used compounds [13]. The recovery of HFCs is of special interest in refrigeration, air conditioning, and heat pumps (RACHP) old equipment when they are reaching their end-of-life and contain HFCs [14]. HFCs Regulation has a mandatory requirement for the old HFCs to be recovered and latter re-used [15]. In some cases, HFCs are partially recovered by adsorption on activated carbons, cryo-condensation, or membrane separation for their re-use in different processes, being all of them highly expensive technologies [16]. Another contaminant whose emissions are important in the solvent industry is acetone. It is widely applied in paint, polymers processing, or pharmaceutical industry being classified as volatile organic compound (VOC) and also contributing to global warming [17]. Moreover, the acetone release to the atmosphere can cause problems to the human respiratory system, skin, and eyes [18]. Therefore, it is important to eliminate VOCs prior to their emissions. Traditionally, this removal has been accomplished by absorption, adsorption, catalytic combustion, or photocatalysis. The most extended is the absorption operation, and research efforts have been conducted to seek less environmentally harmful solvents, usually with high boiling point and low vapor pressure [17]. The removal of other gasses is also crucial in the development of more sustainable processes. For instance, hydrogen sulfide (H_2S) is a toxic gas present in biogas, natural gas, liquefied petroleum gas, or other industrial gas streams [19]. Therefore, the removal of even traces of H_2S is crucial since its toxicity verge is about 10 ppm. In addition to its toxic character, H_2S can also be used as an important feedstock for the productions of sulfur, hydrogen, and some value-added metal sulfides, among others [19]. Depending on the concentration of H_2S in the stream to treat, different technologies have been developed such as absorption, adsorption, membrane separation or biological removal [20]. All of them present some disadvantages on their use mainly attributed to high investment costs or strongly dependent on H_2S concentration [20]. On the other hand, ammonia (NH_3) plays an essential role in the global nitrogen cycle [21], coming from different natural or anthropogenic sources. Since 1900s human activities have caused a great impact on nitrogen cycle, being fossil fuel burning and the use of fertilizers the most important. However, NH_3 emissions are also associated with the chemical industry and related processes (fertilizers production, chemical synthesis, petrochemical processes or wastewater treatment, among others) [22]. The presence of NH_3 in the atmosphere can cause respiratory tract, eye, or skin lesions [21]. Therefore, its removal is important and traditionally accomplished by solid adsorption, liquid absorption, membrane contactors and catalytic reductions. All these technologies require high investment costs derived from the equipment's low efficiencies, or corrosion problems [23]. Finally, in this study the use of bio-ionic liquids for liquid-liquid extraction processes is also considered. Industrial separations based on liquid-liquid extraction play an important role in the petrochemical industry, including hydrocarbon separations, such as aromatic/aliphatic (separation of BTX from reformer and pyrolysis gasolines) [24], benzene/cyclohexane and cyclohexene/cyclohexane since they are together on their production [25,26]. These separations are commercially accomplished in the industry by Sulfolane process by means of liquid-liquid extraction or extractive distillation [26]. In the last decades, new separation processes are being investigated trying to overcome the problems of traditional processes such as solvent losses. More than the separation of refinery streams and/or hydrocarbon-based systems, the quality of liquid fuels is currently investigated by using liquid-liquid extraction processes, in order to control benzene and N- and S- containing aromatics such as pyrrole and thiophene, respectively [27,28]. The last separation-related application of bio-ionic liquids contemplated in this work is the removal of contaminants (phenolic compounds) from water, [29]. This task was traditionally not easy including different technologies such as adsorption, chemical oxidation, or membrane separation. However, some drawbacks like high cost, low efficiencies and the generation of toxic residues are associated to these technologies. Therefore, liquid-liquid extraction emerged as an alternative, trying to look for hydrophobic solvents that can efficiently separate phenolic compounds from water [29].

For all the afore mentioned separation processes, ionic liquids (ILs) have been proposed in literature as potential solvents. Ionic liquids are liquid salts formed by a cation and an anion with melting points below 100 °C [30]. Their excellent properties as solvents such as low vapor pressure, which means null volatility, high solvent capacity, high thermal and chemical stability, among others, attracted the scientific community attention to substitute traditional ones [31]. Moreover, the possibility of tuning the cation and/or the anion for specific applications make them be considered as "designer solvents" [32]. ILs have been widely investigated in CO_2 [33] and H_2S capture [33], HFC removal [13] and recovery in refrigeration cycles [12], acetone [34], or ammonia [35], and in aromatic/aliphatic separation by means of liquid-liquid extraction [36]. However, the initial statement of ILs low toxicity was shown to be incorrect [37]. Therefore, the search of nontoxic and easy biodegradable ILs has been a challenge of the scientific community in last decades.

Biocompatible ionic liquids (bio-ILs) refer to an eco-friendly family of ILs [38]. The synthesis of these compounds involves the selection of both anion and cation derived from biocompatible materials, such as carboxylic acids [39], amino acids [40], glucose [41], among others. These compounds have emerged as a most sustainable approach for the development of new green processes. Most part of the bio-ILs research up to date have been focused on protein-derived amino acid cations and/or anions since they are nontoxic, easily biodegradable, and biocompatible [38]. Moreover, these molecules are abundant in nature at low-cost, which implies even more interest in their use. Big efforts have been made on developing new families of bio-ILs but it remains being a challenge since they are very restricted to an exclusive family of compounds. In fact, cholinium cation has emerged as the most effective approach for "greener" compounds since it comes from natural sources, and it is demonstrated to be easily biodegradable and with low toxicity [42]. Bio-ILs have been successfully proved in different applications of electrochemical and biomedical fields [38]. Even though a chemical will have the same properties irrespective of which resources were used to produce them, in the case of choline based solvents (both ionic liquids and eutectic solvents) it has been claimed that they are more bio-compatible, more bio-degradable and less toxic than their counterparts [38]. Therefore, to highlight these issues, we are using the term bio-based IL-solvents.

The aim of this work is to evaluate a wide variety of bio-ILs (50) as alternative "greener" solvents in industrial separation pro-

cesses by means of COSMO-RS methodology. All selected bio-ILs present choline as common cation due to its favorable environmental concerns. Moreover, comparison with the most promising conventional ILs published in the literature is also presented. Traditional separations are divided into gas absorption to remove GHG contaminants such as CO_2, H_2S, VOCs, or NH_3, and to recover HFCs used in absorption refrigeration cycles like R-134a, R-125, and R-32. Henry's law constants are calculated as thermodynamic parameter of reference. Then, traditional separations by liquid-liquid extraction are also evaluated depending on the bio-IL properties. Octanol-water partition coefficient calculations are calculated to anticipate the hydrophobicity of bio-ILs and their application on extraction of aqueous streams. Finally, hydrocarbon separation processes by liquid-liquid extraction such as aromatic/aliphatic, cyclohexene/cyclohexane, desulfurization, and denitrogenation by using selected bio-ILs are also analyzed by means of liquid-liquid equilibrium data calculations.

2. Computational details

2.1. Molecular geometry optimization

The 50 anions and [choline]$^+$ cation geometries were optimized until their minimum state of energy using Turbomole 7.4 software. Moreover, those solutes that do not exist in COSMO databases (thiophene and hydrogen sulfide) were also optimized using the same program package. In all cases, the geometries calculations were conducted until their minimum energy using the solvent effect (COSMO continuum solvation method) through def-TZVP basis set and DFT/BP86 computational level. Last, it was checked that no negative vibrational frequencies were found by a single point calculation. All the information needed to perform COSMO-RS calculations using COSMOthermX is stored in the generated *.cosmo files.

2.2. COSMO-RS calculations: Henry's law constants, octanol-water partition coefficient, and extractive properties

COSMO-RS method (Conductor-like Screening Model for Real Solvents) is used for calculations in COSMOthermX software. It consists of an *a priori* approach, in which no experimental data is needed for estimations, enabling the prediction of thermodynamic properties by the only use of quantum-chemical calculations. This methodology has been applied in several cases as a preliminary tool to avoid the long and cost demanding experimental tests, selecting, and designing new solvents for specific applications. It was successfully employed in aromatic/aliphatic separations, CO_2 [33], H_2S [33] or acetone absorption [34], among others. COSMOtherm v.19 software with its implicit parametrization BP_TZVP_19 was used for all the calculations of this work. First, for gas absorption phenomena, Henry's law constants (K_H) are used as parameter of reference. K_H is calculated by COSMO-RS following the Eq. (1):

$$K_H = \gamma_i^\infty \cdot p_0^{sat} \tag{1}$$

Where K_H is calculated by the product of γ_i^∞, which is the activity coefficient of the solute at infinite dilution in the bio-IL (calculated by COSMO-RS method) and p_0^{sat} is the vapor pressure of the pure solute of interest (experimental data and dependence with the temperature for each solute). The vapor pressure of the solutes used in this work are found in R-134a [43], R-32 [44], R-125 [45], acetone [46], ammonia [47], CO_2 [48] and H_2S [47]. Moreover, Table S1 of the Supplementary Material includes the Antoine's equation parameters of each solute used for vapor pressure computation at 298 K. In all cases, calculations are made considering the bio-IL as independent ions (C + A model) and a given temperature of 298 K.

Then, the excess Gibbs energy (G^E) and enthalpy (H^E) of the equimolar solute/bio-ILs mixtures are calculated by a vapor-liquid calculation (COSMOtherm software) at 298 K. It is possible to compute the detailed intermolecular interaction contributions to the excess enthalpy by selecting the extended options of the calculation. Thus, the sum of these contributions gives as result the total excess enthalpy (H^E) Eq. (2).

$$H^E = H^E(MF) + H^E(HB) + H^E(vdW) \tag{2}$$

Where $H^E(MF)$ is the contribution related to misfit or electrostatic forces; $H^E(HB)$ is the one attributed to hydrogen bonding; and $H^E(vdW)$ is referred to Van der Waals forces.

The entropic contribution ($-T \cdot S^E$) to the excess Gibbs energy was also calculated following the equation:

$$G^E = H^E - T \cdot S^E \tag{3}$$

Anion's octanol-water partition coefficients at infinite dilution were calculated by a logP/logD calculation (partition coefficient) in COSMOtherm. To do so, it is necessary to include both octanol, water, and anions into the calculation procedure. The cation was omitted on calculations since it is common for all the selected bio-ILs.

Finally, extractive properties for liquid-liquid extraction [distribution ratio (Eq. (4)) and selectivity (Eq. (5))] are calculated by means of activity coefficients at infinite dilution as presented in Eq. (4) and 5. Activity coefficients at infinite dilution are calculated by liquid-liquid equilibrium calculation as implicit in COSMOtherm software and selecting the compositions required for each phase (extract or raffinate).

$$D_2 = \frac{x_2^E}{x_2^R} = \frac{\gamma_2^R}{\gamma_2^E} \tag{4}$$

$$S_{2,1} = \frac{D_2}{D_1} = \frac{\frac{\gamma_2^R}{\gamma_2^E}}{\frac{\gamma_1^R}{\gamma_1^E}} \tag{5}$$

Where x_i^E and x_i^R are the molar fractions of toluene, benzene, cyclohexene, pyrrole, or tiophene (2) or aliphatic compound, i.e., heptane, cyclohexane (1) in the extract (E) and raffinate (R) liquid phases, respectively. γ_i^E and γ_i^R are referred to the activity coefficient at infinite dilution of toluene, benzene, cyclohexene, pyrrole, or tiophene (2) or aliphatic compound, i.e., heptane, cyclohexane (1) in the extract (E) and raffinate (R) liquid phases, respectively.

3. Results

3.1. Gas absorption

First, 50 bio-ILs were selected from the literature [38,49,50]. In all cases, the common cation was [choline]$^+$ and different anions were considered divided into different groups from their precedence: amino acid and carboxylic acid. The complete list of bio-ILs, structures, complete name, CAS number and molecular weight can be found on Table S2 of the Supporting Material. Henry's law constants were selected as thermodynamic parameter of reference in gas absorption application. The capability of COSMO-RS method (specifically COSMOtherm v.19) to predict reasonably good all the solutes involved in this work is presented on Figure S1 of the Supporting Material. Moreover, Table S3 (Supplementary Material) shows all the collected data of Figure S1 with absolute and relative deviations. Once again, it is reaffirmed the good predictions obtained with relative errors below 22% in all cases.

Seven different relevant gasses in the chemical industry were selected for the evaluation of bio-ILs as potential physical absorbents. Table 1 shows the K_H of solutes of interest in the 50 bio-ILs. Color green denotes favorable K_H (low value) and red unfavorable ones (high value), being the orange the intermediate cases.

Table 1

Henry's law constants (bar) of refrigerants, acetone, ammonia, CO_2 and H_2S in the selected 50 choline-based bio-ILs calculated with COSMO-RS method at 298 K.

ILs	R-134a	R-32	R-125	H_2S	CO_2	Acetone	NH_3
	K_H (bar)						
bicarbonate	0.63	3.36	0.69	1.48	14.37	0.13	1.34
glycinate	1.07	4.38	1.13	1.69	18.80	0.20	2.31
acetate	1.18	4.64	1.20	1.65	18.84	0.18	2.26
dihydrogen-phosphate	1.27	4.96	1.70	2.36	22.32	0.22	0.87
methylsulphonate	1.29	4.35	2.30	1.93	23.14	0.28	0.89
glutamate	2.47	5.86	4.00	2.74	26.82	0.30	1.81
asparaginate	2.62	6.18	4.52	2.90	26.95	0.33	1.77
lysinate	2.71	6.70	3.75	2.71	28.36	0.30	2.06
alaninate	2.73	6.78	3.87	2.56	29.00	0.30	2.10
propanoate	2.73	6.94	3.49	2.40	28.13	0.26	2.13
prolinate	3.12	7.65	4.01	2.64	31.08	0.28	2.07
serinate	3.37	7.11	6.11	3.06	33.42	0.36	1.71
glutaminate	3.46	7.33	5.92	3.25	30.20	0.35	1.83
phenylalaninate	3.91	7.30	6.35	2.84	28.20	0.29	1.75
butanoate	4.13	8.53	5.76	2.91	33.29	0.28	1.97
valinate	4.25	8.39	6.67	3.14	33.75	0.31	1.81
aspartate	4.27	7.37	9.55	3.56	36.26	0.40	1.38
succinate	4.29	6.94	13.35	3.30	39.03	0.47	0.48
methioninate	4.37	7.78	7.65	3.57	31.57	0.31	1.73
sinapinate	4.67	7.39	8.73	3.03	29.58	0.27	1.28
maleate	4.67	8.24	10.14	3.66	40.50	0.46	0.83
leucinate	4.74	8.92	7.62	3.39	34.61	0.30	1.67
methylsulphate	4.76	7.19	16.48	3.63	41.59	0.51	0.34
tiglate	4.79	8.64	7.64	3.11	32.97	0.30	1.80
abietate	4.98	9.46	6.30	3.74	24.71	0.14	1.39
decanoate	5.18	10.43	6.25	3.60	31.51	0.20	1.64
tartarate	5.24	9.26	10.54	4.52	49.51	0.46	0.81
neodecanoate	5.24	10.30	6.64	3.71	31.75	0.20	1.60
isoleucinate	5.85	9.94	9.25	3.68	36.88	0.28	1.70
histidinate	5.98	8.24	14.25	3.83	32.91	0.37	1.39
argininate	6.18	9.42	11.93	4.47	33.80	0.37	1.71
malate	6.78	9.67	18.22	4.60	53.81	0.54	0.60
threoninate	7.06	9.44	18.40	4.21	44.29	0.44	1.18
[NTf2]	8.60	8.97	36.55	5.73	40.23	0.08	0.02
tryptophanate	8.71	10.18	18.93	4.29	32.79	0.28	1.27
Tyrosinate	8.84	10.72	20.20	4.70	40.68	0.36	0.96
D-glucuronate	9.41	11.34	28.53	6.16	64.42	0.65	0.47
fumarate	9.53	11.38	26.51	4.99	56.32	0.56	0.64
saccharinate	9.80	9.18	40.80	4.19	42.04	0.42	0.35
ascorbate	9.82	10.85	30.03	5.75	58.88	0.45	0.65
D-quinate	9.92	11.75	28.27	5.87	62.81	0.51	0.61
acesulfamate	12.12	9.87	58.17	5.51	49.59	0.44	0.27
bitartrate	12.38	11.98	49.41	6.21	73.94	0.76	0.32
D-galactouronate	10.52	10.17	40.46	5.70	62.17	0.46	0.42
caffeate	13.66	12.96	34.99	5.85	49.47	0.37	0.72
salicylate	15.15	11.75	58.03	5.17	48.08	0.37	0.64
dihydrogencitrate	18.13	13.38	87.15	7.51	87.76	0.54	0.11
ferulate	20.29	13.36	91.21	6.37	49.23	0.27	0.17
2,5-dihydroxybenzoate	26.76	16.33	119.17	8.51	71.01	0.54	0.42

First, it can be observed that the trend in the refrigerant gasses is the same for the selected bio-ILs. The lowest K_H are found in the case of R-134a followed by R-125 and R-32, in good agreement with previous work on the literature [13]. It is important to point out the wide ranges of values found for the three cases. This implies that the proper selection of the bio-IL as potential refrigerants absorbent is crucial. In the case of R-134a and R-32, the range covers two orders of magnitude whereas in R-125, the differences are from 0.7 to 120 bar. In all cases, the smallest polar anions are those showing the best results, for instance bicarbonate, glycinate, ac-

etate. Moreover, it seems that anions containing phosphate groups may also act as good refrigerant absorbents. The different selected anions can be divided in three great groups depending on their source: amino acids, carboxylic acids (blue) and phosphate based (orange). It seems that the gas absorption is being dominated by the size of the anion, where the small ones are those exhibiting the best behavior. This is in good agreement with previous conclusions reported on the literature [12]. This fact is also reflected on carboxylic acids derived (blue), because while increasing the non-polar alkyl chain of the anion, K_H values become higher. Regard-

ing the amino acid group, similar conclusions can be drawn, being those small anions exhibiting the best performance. However, phosphate-based anions appear as a good alternative for the task. Refrigerant's solubility is enhanced when fluor atoms are incorporated to the IL (cation and/or anion) structure, reporting K_H values from 1 to 2 bar [13,51,52]. Therefore, it seems that at least 4–5 bio-ILs selected in this work may be competitive with actual proposals. Moreover, in sight of the obtained K_H values, it is clearly seen that bio-ILs can also be used to efficiently separate R-134a from R-32 with high selectivity values (2–5 in molar terms), and even higher than those reported [13].

Acid gasses were also evaluated (H_2S and CO_2). Starting with hydrogen sulfide, it can be observed a narrow range between 1.5 and 8.5 bar. It is remarkable the difference between this range and that previously seen in the refrigerant gasses, being notoriously narrower. Similar conclusions can be obtained than in previous cases, being carbonates of short chain anions the ones exhibiting the best performance. Moreover, the increase in the alkyl chain leads to lower solubilities. Phosphate-based anions also report a favorable physical contribution to the aforementioned gas absorption. In the case of amino acids, different behaviors are clearly seen, being those small anions presenting low K_H (i.e., favorable absorption), whereas big ones exhibit a worse performance. The IL [emim][MePO$_3$] is reported as good H_2S physical absorbent with a K_H value of 1.12 bar. As seen in Table 1, no bio-ILs are reported presenting lower values but some of them may be competitive in terms of K_H, such as bicarbonate (1.5 bar), or glycinate (1.7 bar). Regarding CO_2, physical absorption, K_H are shown in Table 1. The range comes from 14 to 70 bar. Therefore, the same as H_2S solute, the range of K_H is narrower than other cases, so the selection of bio-ILs should move to those presenting chemical absorption. In the case of CO_2, the promotion of Van der Waals forces would imply higher solubilities. However, the anions involved in the selected bio-ILs do not promote this type of interactions. It is seen how acetate anion family is the one exhibiting the best behavior, being short alkyl chain the best for the task. It is also seen how phosphate-based anions also exhibit reasonably good K_H values for CO_2 physical absorption, that may be potential candidates for such absorption process. Regarding amino acid-based anions, again the smallest ones present a better performance. These results can be compared with [bmim][acetate] IL, which is the IL used as reference for this absorption process. The physical contribution gives a K_H value of 23 bar [33], which means that at least 2–3 bio-ILs may be competitive in terms of K_H respect to the benchmark (the IL reported as reference to be the best candidate in the literature). It is known that some of the proposed bio-ILs may present chemical absorption by these two gasses [53,54]. However, the aim of this work is to contextualize bio-ILs as "greener" solvents for conventional physical absorption and compare results with typical ILs used. Future work will be conducted on evaluating the best bio-ILs here proposed as H_2S, and CO_2 chemical absorbents based on DFT calculations and experimental tests.

In addition to the criteria commented above, it is important to check the toxicity of these bio-ILs, being bicarbonate anion the one with the lowest toxicity values compared to the rest of solvents evaluated [55]. Therefore, it can also be used as additional criteria for the selection of bio-ILs for the different separation processes.

Acetone was selected as VOC of reference, and its results are presented on the sixth column of Table 1. In this case, it can be observed that differences on K_H are lower than in previous cases, having a narrow range of values with one order of magnitude of difference. Moreover, comparing the obtained results with the refrigerant ones, K_H values are notoriously lower (from 0.08 to 0.8 bar), indicating a more favorable physical absorption. It is known that the cation is playing a crucial role on acetone solubility in ILs [34]. In this case, the common cation is [choline]$^+$ that

can act as hydrogen bond donor with the oxygen atoms of acetone. Therefore, it seems that those big anions with dispersed charge, as [NTf$_2$]$^-$, lacking hydrogen bond acceptor ability are the best for the task. Regarding the anion, long chain carboxylic acids contribute to increase acetone solubility in bio-ILs. It is important to look for anions presenting lower interactions with [choline]$^+$ than acetone, forming hydrogen bonds between cation-solute, rather than competitive cation-anion interactions. The obtained K_H values can be compared with the conventional IL reporting the best performance which is [bpyr][NTf$_2$] [34], with K_H of 0.03 bar, slightly below than [choline][NTf$_2$] value but in the same order of magnitude. This means that at least one bio-IL can be competitive in terms of K_H with the best reported in the literature.

NH_3 is the last solute of Table 1, with K_H values ranging from 0.02 to 2.5 bar, exhibiting an intermediate behavior between the solutes previously analyzed. According to the conclusions reported in the literature, the cation plays a dominant role on NH_3 absorption by ILs [21]. Specifically, those cations functionalized with -OH groups, as in the case of [choline]$^+$, significantly enhance NH_3 solubility in ILs when compared to their analogues without functionalization [35]. Therefore, cations with acidic character will lead to higher NH_3 physical absorption. Regarding the anions, Table 1 shows that big anions with delocalized charge, such as [NTf$_2$]$^-$, enhance the behavior of the bio-IL, in good agreement with the literature [35]. In sight of the results of Table 1, the same conclusions as in the case of acetone can be drawn, being those big carboxylic-based or amino acid-based anions, with lower polarity, the ones presenting the best performance. Once again, the cation dominates the solubility, so it is crucial to find anions that enable the cation to interact with the solute, avoiding competitive cation-anion interactions. The obtained results can be compared with those previously published. For instance, a K_H value of 4 bar was reported for [emim][NTf$_2$] [56], and 0.05 bar for [choline][NTf$_2$] [35]. In this case, it is reaffirmed that [choline][NTf$_2$] is the best bio-IL for the task.

In sum, thanks to COSMO-RS methodology, it is possible to put on the map bio-ILs as absorbents for different gas separations of the chemical industry. Moreover, some of them show a potential good performance for the solutes analyzed.

Fig. 1 shows the excess properties for equimolar mixtures for the best solute/bio-IL pair in each case. Fig. 1A reveals the Gibbs energy in terms of the enthalpic and entropic contributions, where different trends are observed. In the cases showing a more thermodynamically favored mixing behavior (NH_3, H_2S, and acetone), the enthalpic contribution governs the absorption process. This is explained by the ability of forming hydrogen bonds between gas solute and bio-IL (see the orange bar on Fig. 1B). The rest of the cases are dominated by the entropic contribution, with increasing Gibbs free energy, disfavoring the solute-solvent mixture. This fact is also reflected in Fig. 1B, which presents the different contributions (misfit, Van der Waals, and hydrogen bonding) to the excess enthalpy. As mentioned before, the cases in which the enthalpic contribution govern the process are controlled by the formation of strong hydrogen bond interactions. The other cases are controlled by weaker electrostatic forces (Misfit), and that is the main reason that enthalpic contribution is not governing the absorption process.

3.2. Liquid-liquid extraction

Next stage involves the application of selected bio-ILs in liquid-liquid extraction separations of relevance in the chemical industry. They can be divided in separations of solutes (i.e., contaminants or value-added compounds) from aqueous streams and hydrocarbon separations.
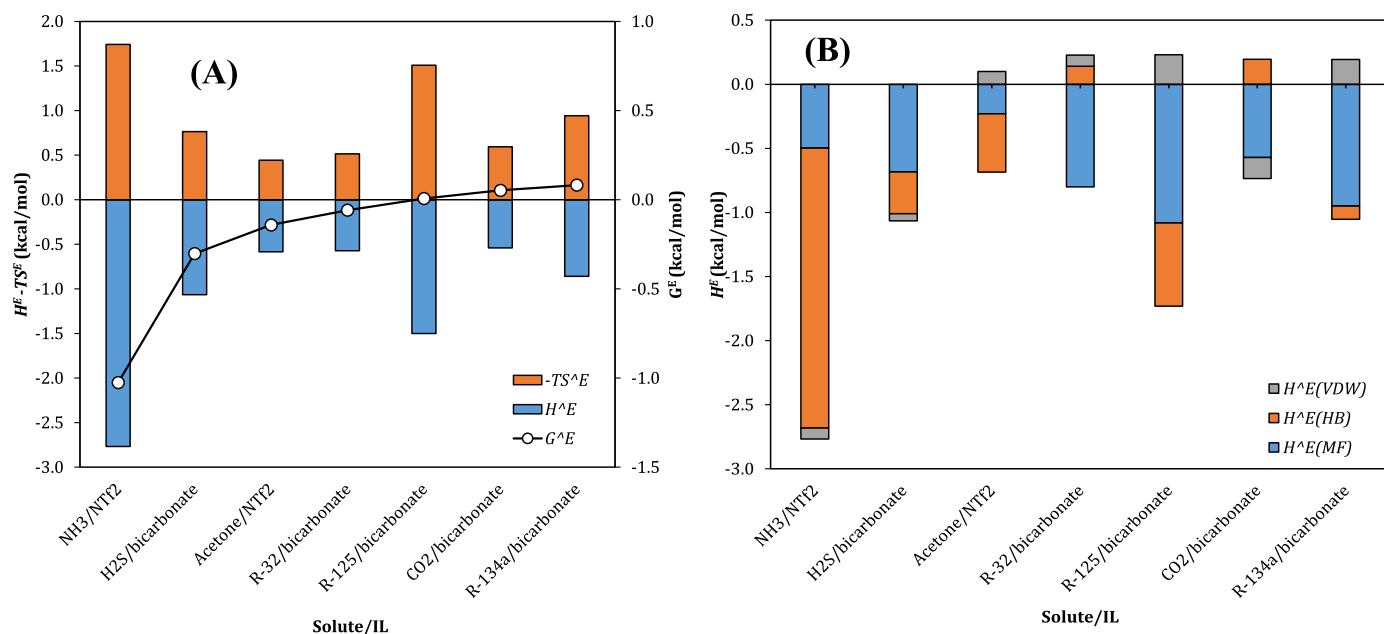
Fig. 1. **(A)** Excess energies (enthalpy, entropy, and Gibbs) of solute/bio-IL exhibiting the best performance in terms of K_H and **(B)** contributions to excess enthalpy of each solute/bio-IL pair calculated with COSMO-RS method at 298 K.

3.2.1. Aqueous streams

The formation of two liquid phases when separating solutes of interests from aqueous streams is essential. Therefore, before analyzing the extractive properties, the first step is to find bio-ILs with hydrophobic character. To do so, octanol-water partition coefficient was calculated with COSMO-RS method for the 50 anions. The results are shown in Fig. 2, indicating that most part of the anions, and especially those based on amino acid, presents K_{OW} below 1 (miscible in water), which means that they are completely hydrophilic. This is in good agreement with conclusions reported in the literature [57]. From all the selected anions only 2,5-dihydroxybenzoate shows K_{OW} higher than 1, which would imply a smooth hydrophobic character. $[NTf_2]^-$ anion shows an intermediate behavior, but it is usually taken as hydrophobic anion of reference in the literature [58,59]. Moreover, Figure S2 of the Supplementary Material shows the K_{OW} of the 50 bio-ILs (including the cation in calculations). As seen, the results show bio-ILs with hydrophilic character in all cases with lower K_{OW} values when considering [choline] in calculations. Therefore, separations of solutes from aqueous streams would only take place by using these two bio-ILs, that present the ability of forming two liquid phases. It was decided not to calculate the extractive properties of the selected bio-ILs, since only these two can be used in practical applications. Moreover, LLE calculations were made with COSMO-RS method, without finding two liquid phases in any case. Consequently, future works should be conducted on finding bio-ILs with hydrophobic properties for aqueous separations.

3.2.2. Aromatic-aliphatic separation and denitrogenation and desulfurization of liquid fuels

Table 2 shows the calculated extractive properties (distribution coefficient and selectivity) of selected bio ILs for different mixtures of interest in the industry: toluene/heptane as hydrocarbon mixture reference of dearomatization; tiophene/heptane as desulfurization process; and pyrrole/heptane as denitrogenation process. On the other hand, benzene/cyclohexane and cyclohexene/cyclohexane COSMO-RS results can be found on Table S3 of the Supplementary Material. In all cases, it was checked that two liquid phases are formed with the aliphatic compound. LLE point

compositions are shown in Table S4 of the Supplementary Material. In all the mixtures evaluated, partition coefficients and selectivities present an opposite trend, i.e. those bio-ILs providing higher partition coefficient are those with lower selectivity and vice versa, as it was already found with common ILs [60]. Starting with toluene/heptane mixture, distribution coefficients range are from 0.03 to 2.5. Therefore, it seems that the selection of the proper anion would imply better separations. In general, small anions exhibit the best performance among the bio-ILs evaluated, whereas more voluminous anions lead to worse separations. An opposite trend is found when observing selectivity values with a range between 2.7 and 52.5 for the best case. In this case, it seems that interactions between $[NTf_2]^-$ and aromatics is weaker and more selective when $[choline]^+$ is present [60]. In the case of desulfurization (tiophene/heptane), the results are completely analogous, being those bio-ILs exhibiting the best performance the same as in the previous case: acetate-based and phosphate-based anions in terms of partition coefficients and $[NTf_2]$, benzoate and amino-acid based in terms of selectivities. On the other hand, the range is different, with values between 0.2 and 6.4 in terms of partition coefficients, which would mean that separation in this case is more favored. Selectivity range are from 2.5 to 142, being those hydrophobic anions, the ones exhibiting once again the best performance, in good agreement with previous conclusions [27,28]. In the case of denitrogenation with pyrrole/heptane mixtures, the ranges are quite different, having partition coefficients from 18 to 750 and selectivity from 40 to 2000, which means that the separation is very favored by the presence of bio-ILs. The evolution of extractive properties in the aromatic/heptane separation clearly correlates to toluene < benzene < thiophene < pyrrole, as previously stated in the literature, so one system can be used to preliminary select a proper IL to all separations [61].

Same conclusions can be extracted from the other mixtures, being the bio-ILs performance order almost the same; acetate-based anions are the best candidates in terms of partition coefficients and amino-acid based, and benzoate, the best in terms of selectivities. Fig. 3 presents the Gibbs energy and entropic and enthalpic contributions for [choline][bicarbonate] (best in terms of partition coefficient Fig. 3A) and [choline][2,5-dihydroxybenzoate] (best in
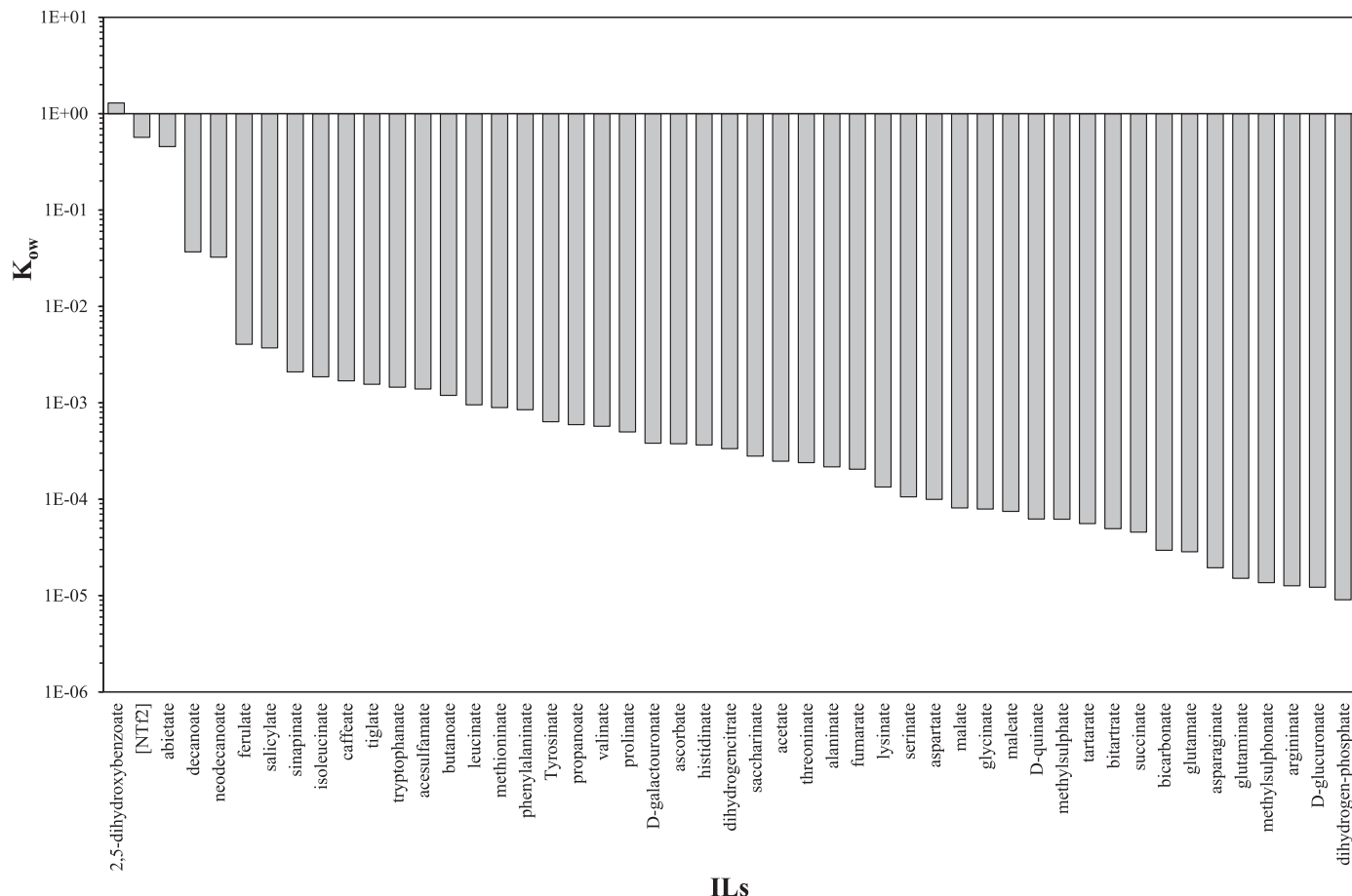
Fig. 2. Octanol-water partition coefficient of 50 selected anions calculated with COSMO-RS method at 298 K.
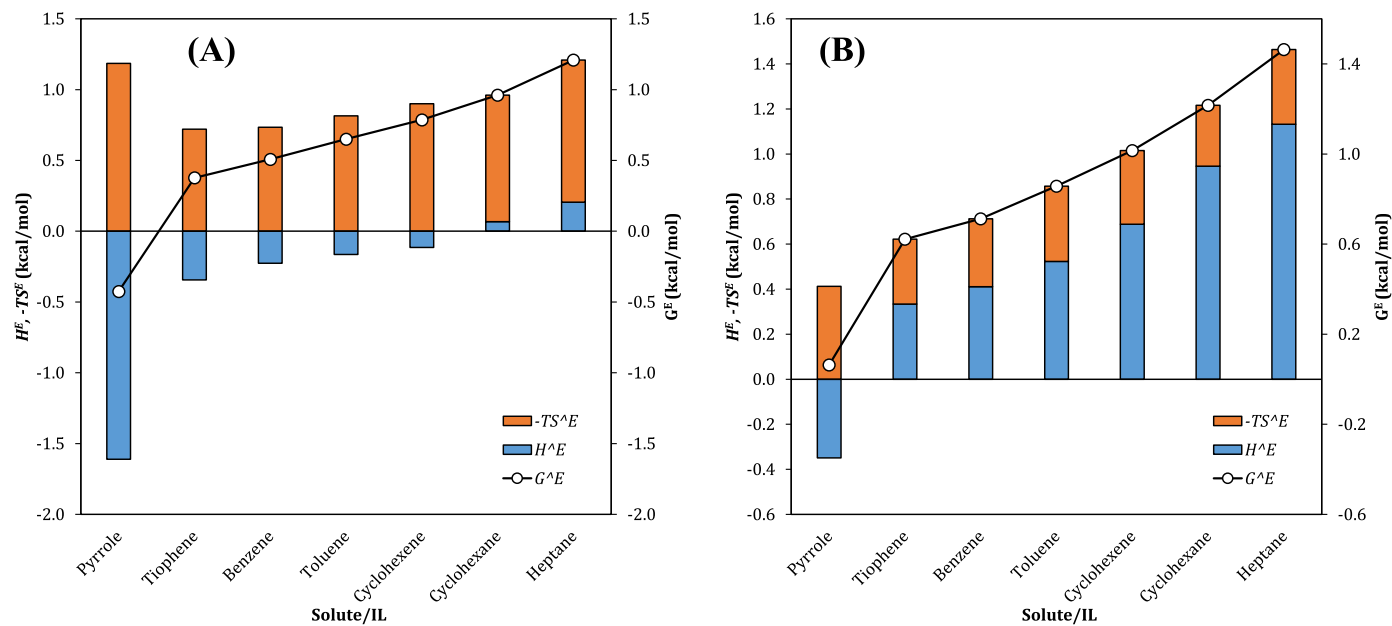

Fig. 3. Excess energies (enthalpy, entropy and Gibbs) of the components involved in the work and the best bio-IL in terms of distribution coefficient [choline][bicarbonate] **(A)** and selectivities [choline][1,5-dihydroxybenzoate] **(B)** calculated with COSMO-RS method at 298 K.

Table 2

Extractive properties (partition coefficients and selectivities) of representative aromatic-aliphatic, denitrogenation and desulfurization mixtures in the 50 selected choline-based bio-ILs calculated with COSMO-RS method at 298 K.

ILs	Partition Coefficient (D₂)			Selectivity (S₂,₁)		
	Toluene-heptane	Tiophene-Heptane	Pyrrole-Heptane	Toluene-heptane	Tiophene-Heptane	Pyrrole-Heptane
2,5-dihydroxybenzoate	0.03	0.19	18.70	52.52	142.14	1950.67
dihydrogencitrate	0.02	0.18	19.83	49.45	134.55	2035.05
acesulfamate	0.04	0.34	30.91	44.71	122.12	1545.81
[NTf2]	0.07	0.43	13.59	41.80	94.71	421.34
salicylate	0.05	0.35	38.58	41.67	103.06	1564.29
ferulate	0.05	0.32	22.26	41.04	93.15	914.53
saccharinate	0.06	0.47	42.34	35.99	99.50	1261.11
bitartrate	0.03	0.25	30.65	35.09	101.05	1738.38
D-galactouronate	0.05	0.30	35.43	31.48	71.17	1162.22
caffeate	0.07	0.39	44.32	25.81	51.71	829.46
fumarate	0.06	0.40	52.80	23.64	54.61	1007.34
ascorbate	0.06	0.35	41.87	22.98	46.37	783.21
D-glucuronate	0.05	0.29	38.55	20.21	43.54	801.45
threoninate	0.08	0.46	73.62	19.93	38.97	873.94
tryptophanate	0.11	0.52	73.62	19.60	34.75	681.24
D-quinate	0.06	0.29	40.97	19.46	37.30	725.93
methylsulphate	0.10	0.66	69.81	18.78	45.65	668.19
histidinate	0.11	0.57	84.71	18.70	35.95	747.29
Tyrosinate	0.09	0.46	62.75	18.40	33.25	632.13
malate	0.08	0.47	62.64	17.99	37.47	695.29
succinate	0.12	0.73	82.61	16.06	35.86	568.66
argininate	0.10	0.47	87.31	15.68	26.47	687.99
aspartate	0.14	0.71	113.37	15.07	27.93	619.88
sinapinate	0.19	0.90	127.27	13.92	23.68	464.27
maleate	0.14	0.74	101.28	13.41	26.04	493.68
methioninate	0.16	0.68	119.50	12.65	19.80	488.20
tartarate	0.13	0.62	85.02	12.18	20.81	400.26
tiglate	0.19	0.84	160.00	11.82	18.66	497.53
isoleucinate	0.16	0.61	123.68	11.48	16.02	451.95
phenylalaninate	0.20	0.87	160.91	11.27	17.98	465.79
serinate	0.19	0.86	161.17	10.79	17.32	453.41
glutaminate	0.18	0.79	145.68	10.44	16.44	420.01
valinate	0.19	0.77	155.91	10.41	15.34	435.10
butanoate	0.23	0.93	205.70	10.18	14.60	448.97
leucinate	0.18	0.70	131.36	10.16	14.52	381.46
asparaginate	0.24	1.04	180.18	9.52	14.74	356.78
glutamate	0.28	1.19	218.60	9.42	14.28	365.33
alaninate	0.29	1.16	244.07	8.42	12.00	352.53
propanoate	0.36	1.39	301.48	8.20	11.26	341.39
lysinate	0.24	0.91	208.07	7.83	10.54	337.07
prolinate	0.27	1.01	231.39	7.78	10.46	332.73
neodecanoate	0.25	0.76	125.60	6.75	7.38	169.56
decanoate	0.26	0.79	133.84	6.59	7.18	168.57
methylsulphonate	0.56	2.28	286.44	5.62	8.28	145.17
abietate	0.37	1.00	110.83	5.54	5.39	83.31
acetate	1.05	3.27	647.22	4.61	5.15	142.21
glycinate	0.95	2.92	584.25	4.30	4.77	132.90
dihydrogen-phosphate	0.96	2.99	316.01	3.74	4.21	61.91
bicarbonate	2.46	6.44	744.69	2.70	2.56	41.20

terms of selectivities Fig. 3B). First, the only negative G^E values are found with bicarbonate and pyrrole, in good agreement with results of Table 2, being the one presenting the highest partition coefficient value. In this case, enthalpic contribution is governing the process due to the hydrogen bonding formation; this is usually found when analyzing proper solvents for aromatic-aliphatic separation [36]. The rest of the cases present less thermodynamically favored mixtures (unfavorable entropic contribution controlling the mixtures), being the aromatics, olefins, and sulfur-containing the ones with lower values compared with aliphatic ones (cyclohexane

and heptane). In the case of 2,5-dihydroxybenzoate, the results are analogous except for pyrrole mixture in which non-spontaneous behavior is found. The fact that this bio-IL is the one presenting the highest selectivity values is confirmed by the most repulsive behavior with aliphatic compounds (heptane, cyclohexane).

Analyzing the excess enthalpy, the use of bio-ILs is demonstrated to be conceptually designable for common separation problems in the industry, ranging from more favorable dearomatization, desulfurization and desnitrogenation of liquid fuels to more challenging benzene/cyclohexane or cyclohexane/cyclohexene sep-
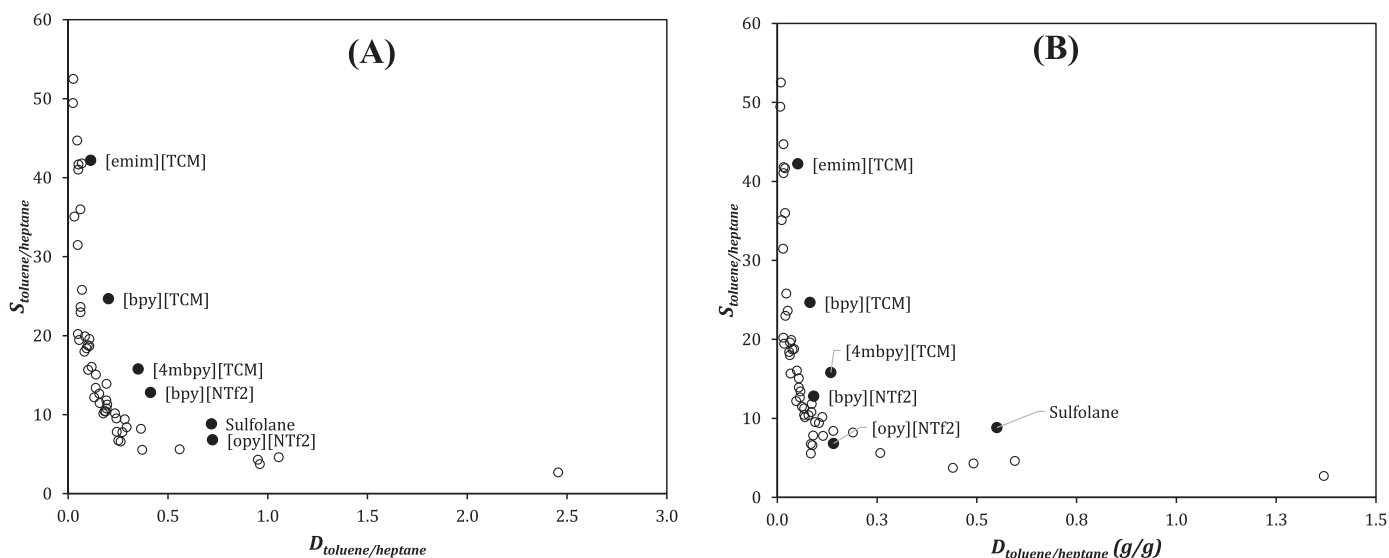
Fig. 4. Toluene/heptane extractive properties of evaluated bio-ILs and some ILs used as reference and sulfolane as benchmark solvent in molar (A) and mass (B) terms calculated with COSMO-RS method at 298 K.

arations, describing similar solvent features as other solvent classes as ILs, eutectic solvents and so on.

Fig. 4 shows the selectivity as a function of the partition coefficient for the case of toluene/heptane mixture (rest of the mixtures can be found in Figure S3 of the Supplementary Material). Toluene/heptane stands out as the benchmark mixture in the aromatic separation from aliphatics since it shows an intermediate behavior, as depicted in Fig. 3, together with representativeness in a wide range of separation cases covering large ranges of aromatic contents and compositions [60]. Figure collects the extractive properties for all the bio-ILs of this work and other ILs selected from literature in molar (A) and (B) mass units. Canales and Brennecke concluded that [TCM] and [NTf$_2$] anions are the more favorable in terms of extractive and physical properties in order to complete with conventional solvents [60]; thus, [emim][TCM], [bpy][TCM], [bpy][NTf$_2$], [opy][NTf$_2$] were selected as representative common ILs and, together with benchmark solvent at industrial scale, sulfolane, stand out as solvents of reference [24]. Rigorous comparison should be made taking partition coefficients in mass terms (B). As seen, the bio-ILs follow a similar trend than that obtained for benchmark solvents in these separations and at least three bio-ILs may be better or at least competitive in terms of selectivity with the most selective ILs selected in the work (especially those presenting low MW). Some other bio-ILs exhibit a high extraction capacity comparing to the reported common ILs with high extraction affinity for toluene, as [4mbpy][TCM], and comparable distribution ratios to NTf$_2$-based ILs, demonstrating that bio-ILs can be proposed as alternative to common ILs for aromatic-aliphatic industrial separations in terms of process efficiency and environmental concerns, especially because of their low MW, which brings them closer to ILs proposed in the literature as good extracting solvents. Moreover, the high number of bio-ILs with highlighted selectivity enables the possibility of using them as entrainers in extractive distillation process, since extractive properties and relative volatilities can be correlated in these kind of systems as demonstrated in the literature [62].

4. Conclusions

In this work, bio-ILs have been evaluated as promising solvents in traditional separations of the chemical industry, including gas absorption and liquid-liquid extraction by means of COSMO-RS methodology. Some bio-ILs for refrigerant gasses absorption show enhanced properties in terms of K_H compared to proposed common ILs on the literature. Bicarbonate-based anion stands out as the best for the task from those evaluated. Regarding acid gasses removal, it was not found any bio-IL showing enhanced behavior compared to [emim][MePO$_3$] reported as good physical absorbent. However, some of the bio-ILs tested (bicarbonate or acetate-based anions) present similar K_H values, which would mean competitiveness with the IL used as benchmark. In the case of CO$_2$, two or three bio-ILs (bicarbonate and glycinate anions) are competitive in terms of physical contribution with [bmim][acetate] IL, widely used as reference in CO$_2$ capture processes. Acetone is selected as VOC of reference, in which [choline][NTf$_2$] stands out as the best candidate, in good agreement with conclusions previously extracted in the literature. In the case of NH$_3$, a similar conclusion can be drawn, being [choline][NTf$_2$] the best for the task. Recovery of contaminants or value-added compounds are also evaluated by means of liquid-liquid extraction. To do so, it is essential to find bio-ILs forming two liquid phases (hydrophobic bio-ILs). In this case, octanol-water partition coefficient calculation shows that LLE is not formed with selected bio-ILs. Hydrocarbon separation, namely dearomatization, denitrogenation, and desulfurization of liquid fuels together with benzene/cyclohexane/cyclohexene separations by means of liquid-liquid extraction are also evaluated, showing that proposed bio-ILs cover the whole range of partition coefficients and selectivities, allowing to select them on a need basis. Comparison with sulfolane (benchmark) and leading common ILs proposed in the literature reflects that at least two or three bio-ILs (benzoate and amino acid-based anions) may be competitive or even better in terms of separation efficiency. Finally, other separations as extractive distillation, not explored in this work, is here opened to this new class of compatible solvents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2022.113495.

References

[1] D.R. Joshi, N. Adhikari, An overview on common organic solvents and their toxicity, J. Pharm. Res. Int 28 (3) (2019) 1–18.

[2] C.J. Clarke, et al., Green and sustainable solvents in chemical processes, Chem. Rev. 118 (2) (2018) 747–800.

[3] S. Abernethy, R.B. Jackson, Global temperature goals should determine the time horizons for greenhouse gas emission metrics, Environ. Res. Lett. 17 (2) (2022) 024019.

[4] R.S. Dimitrov, The Paris agreement on climate change: behind closed doors, Glob. Environ. Polit. 16 (3) (2016) 1–11.

[5] W.F. Lamb, et al., A review of trends and drivers of greenhouse gas emissions by sector from 1990 to 2018, Environ. Res. Lett. (2021).

[6] R. Tuckett, in: *Greenhouse Gases*, in *Encyclopedia of Analytical Science*, Elsevier, 2019, pp. 362–372.

[7] IPCC, Carbon Dioxide Capture and Storage. 2015.

[8] M. Aghaie, N. Rezaei, S. Zendehboudi, A systematic review on CO2 capture with ionic liquids: current status and future prospects, Renew. Sustain. Energy Rev. 96 (2018) 502–525.

[9] Agency, E.E., Fluorinated greenhouse gases 2021. 2021.

[10] K.M. Stanley, et al., Increase in global emissions of HFC-23 despite near-total expected reductions, Nat. Commun. 11 (1) (2020) 397.

[11] Commission, E., Fluorinated greenhouse gases (https://ec.europa.eu/clima/eu-action/fluorinated-greenhouse-gases_en). 2019.

[12] D. Moreno, et al., Absorption refrigeration cycles based on ionic liquids: refrigerant/absorbent selection by thermodynamic and process analysis, Appl. Energy 213 (2018) 179–194.

[13] J.E. Sosa, et al., Absorption of fluorinated greenhouse gases using fluorinated ionic liquids, Ind. Eng. Chem. Res. 58 (45) (2019) 20769–20778.

[14] S. Asensio-Delgado, et al., Absorption separation of fluorinated refrigerant gases with ionic liquids: equilibrium, mass transport, and process design, Sep. Purif. Technol. 276 (2021) 119363.

[15] Environment, R.E., Assessment of the potential to reduce UK F-gas emissions beyond the ambition of the F-gas regulation and Kigali amendment. 2019.

[16] W.-.T. Tsai, H.-.P. Chen, W.-.Y. Hsien, A review of uses, environmental hazards and recovery/recycle technologies of perfluorocarbons (PFCs) emissions from the semiconductor manufacturing processes, J. Loss Prev. Process. Ind. 15 (2) (2002) 65–75.

[17] X. Ma, et al., Comprehensive evaluation of ionic liquid [Bmim][PF6] for absorbing toluene and acetone, Environ. Pollut. 285 (2021) 117675.

[18] R. Natarajan, Performance Evaluation of Biodegradation of Isoprene, Acetone Mixt. Integr. Biofilter 146 (6) (2020) 04020030.

[19] F. Li, et al., Rotten eggs revaluated: ionic liquids and deep eutectic solvents for removal and utilization of hydrogen sulfide, Ind. Eng. Chem. Res. (2022).

[20] Y. Wang, Y. Liu, Y. Wang, Oxidation absorption of hydrogen sulfide from gas stream using vacuum ultraviolet/H2O2/urea wet scrubbing system, Process Saf. Environ. Prot. 140 (2020) 348–355.

[21] J. Tian, B. Liu, Ammonia capture with ionic liquid systems: a review, Crit. Rev. Environ. Sci. Technol. 52 (5) (2022) 767–809.

[22] S.N. Behera, et al., Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, Environ. Sci. Pollut. Res. 20 (11) (2013) 8092–8131.

[23] Q. Jiang, et al., Simultaneous removal of hydrogen sulfide and ammonia in the gas phase: a review, Environ. Chem. Lett. (2022) 1–17.

[24] P. Navarro, et al., Dearomatization of pyrolysis gasoline by extractive distillation with 1-ethyl-3-methylimidazolium tricyanomethanide, Fuel Process. Technol. 195 (2019) 106156.

[25] M. Ayuso, et al., Enhanced separation of benzene and cyclohexane by homogeneous extractive distillation using ionic liquids as entrainers, Sep. Purif. Technol. 240 (2020) 116583.

[26] N. Delgado-Mellado, et al., Imidazolium and pyridinium-based ionic liquids for the cyclohexane/cyclohexene separation by liquid-liquid extraction, J. Chem. Thermodyn. 131 (2019) 340–346.

[27] M.H. Ibrahim, et al., The role of ionic liquids in desulfurization of fuels: a review, Renew. Sustain. Energy Rev. 76 (2017) 1534–1549.

[28] U. Domańska, M. Wlazło, Effect of the cation and anion of the ionic liquid on desulfurization of model fuels, Fuel 134 (2014) 114–125.

[29] E. Skoronski, et al., Use of phosphonium ionic liquids for highly efficient extraction of phenolic compounds from water, Sep. Purif. Technol. 248 (2020) 117069.

[30] J.D. Holbrey, K. Seddon, Ionic liquids, Clean products and processes 1 (4) (1999) 223–236.

[31] C. Chiappe, D. Pieraccini, Ionic liquids: solvent properties and organic reactivity, J. Phys. Org. Chem. 18 (4) (2005) 275–297.

[32] N.V. Plechkova, K.R. Seddon, Ionic Liquids: "Designer" Solvents for Green Chemistry, 105, John Wiley & Sons, Hoboken, 2007.

[33] D. Hospital-Benito, et al., Process analysis overview of ionic liquids on CO2 chemical capture, Chem. Eng. J. 390 (2020) 124509.

[34] E. Ruiz, et al., Interactions of ionic liquids and acetone: thermodynamic properties, quantum-chemical calculations, and NMR analysis, J. Phys. Chem. B 117 (24) (2013) 7388–7398.

[35] J. Palomar, et al., Task-specific ionic liquids for efficient ammonia absorption, Sep. Purif. Technol. 82 (2011) 43–52.

[36] E. Hernández, et al., Multiscale evaluation of CO2-derived cyclic carbonates to separate hydrocarbons: drafting new competitive processes, Fuel Process. Technol. 212 (2021) 106639.

[37] D. Zhao, Y. Liao, Z.J.C.s. Zhang, air, water, Toxic. Ion. Liq. 35 (1) (2007) 42–48.

[38] J.M. Gomes, S.S. Silva, R.L. Reis, Biocompatible ionic liquids: fundamental behaviours and applications, Chem. Soc. Rev. 48 (15) (2019) 4317–4335.

[39] N. Muhammad, et al., Synthesis and physical properties of choline carboxylate ionic liquids, J. Chem. Eng. Data 57 (8) (2012) 2191–2196.

[40] S. Kirchhecker, D. Esposito, Amino acid based ionic liquids: a green and sustainable perspective, Curr. Opin. Green Sustain. Chem. 2 (2016) 28–33.

[41] L. Poletti, et al., Glucose-derived ionic liquids: exploring low-cost sources for novel chiral solvents, Green Chem. 9 (4) (2007) 337–341.

[42] A. Foulet, et al., Understanding the physical properties, toxicities and anti-microbial activities of choline-amino acid-based salts: low-toxic variants of ionic liquids, J. Mol. Liq. 221 (2016) 133–138.

[43] Goodwin, A.R.H., D.R. Defibaugh, and L.A.J.I.J.o.T. Weber, The vapor pressure of 1,1,1,2-tetrafluoroethane (R134a) and chlorodifluoromethane (R22). 1992. 13: p. 837–854.

[44] Fu, Y.-.D., L.-.Z. Han, and M.-.S.J.F.p.e. Zhu, PVT properties, vapor pressures and critical parameters of HFC-32. 1995. 111(2): p. 273–286.

[45] Ye, F., et al., Gas-phase PVT properties and vapor pressures of pentafluoroethane (HFC-125) determined according to the Burnett method. 1995. 40(1): p. 148–152.

[46] Ambrose, D., C. Sprake, and R.J.T.J.o.C.T. Townsend, Thermodynamic properties of organic oxygen compounds XXXIII. The vapour pressure of acetone. 1974. 6(7): p. 693–700.

[47] D.R. Stull, Vapor pressure of pure substances. Organic and inorganic compounds, Ind. Eng. Chem. 39 (4) (1947) 517–540.

[48] C.E. Bryson, V. Cazcarra, L.L. Levenson, Sublimation rates and vapor pressures of water, carbon dioxide, nitrous oxide, and xenon, J. Chem. Eng. Data 19 (2) (1974) 107–110.

[49] M. Sharma, et al., Syntheses and characterization of few bio-ionic liquids comprising of cholinium cation and plant derived carboxylic acids as anions, J. Indian Chem. Soc. 98 (11) (2021) 100205.

[50] X.-.D. Hou, et al., Effect of anion structures on cholinium ionic liquids pretreatment of rice straw and the subsequent enzymatic hydrolysis, Biotechnol. Bioeng. 112 (1) (2015) 65–73.

[51] J.E. Sosa, et al., Process Evaluation of Fluorinated Ionic Liquids as F-Gas Absorbents, Environ. Sci. Technol. 54 (19) (2020) 12784–12794.

[52] X. Liu, et al., Vapor–Liquid Equilibrium of Three Hydrofluorocarbons with [HMIM][Tf2N], J. Chem. Eng. Data 60 (5) (2015) 1354–1361.

[53] Moya, C., et al., Encapsulated Ionic Liquids for CO2 Capture: using 1-Butylmethylimidazolium Acetate for Quick and Reversible CO2 Chemical Absorption. 2016. 17(23): p. 3891–3899.

[54] Lemus, J., et al., Process analysis of ionic liquid-based blends as H2S absorbents: search for thermodynamic/kinetic synergies. 2021. 9(5): p. 2080–2088.

[55] S.P.M. Ventura, et al., Ecotoxicity analysis of cholinium-based ionic liquids to Vibrio fischeri marine bacteria, Ecotoxicol. Environ. Saf. 102 (2014) 48–54.

[56] T. Turnaoglu, M. Shiflett, The first thermodynamic and kinetic analysis of ammonia in imidazolium based ionic liquids using a gravimetric microbalance, Ind. Eng. Chem. Res. (2019) 58.

[57] P. Pavez, et al., Choline [amino acid] ionic liquid/water mixtures: a triple effect for the degradation of an organophosphorus pesticide, ACS Omega 5 (41) (2020) 26562–26572.

[58] P. Nockemann, et al., Temperature-driven mixing-demixing behavior of binary mixtures of the ionic liquid choline bis(trifluoromethylsulfonyl)imide and water, J. Phys. Chem. B 113 (5) (2009) 1429–1437.

[59] E.J. González, et al., *On the behavior of imidazolium* versus *pyrrolidinium ionic liquids as extractants of phenolic compounds from water: experimental and computational analysis*, Sep. Purif. Technol. 201 (2018) 214–222.

[60] R.I. Canales, J.F. Brennecke, Comparison of ionic liquids to conventional organic solvents for extraction of aromatics from aliphatics, J. Chem. Eng. Data 61 (5) (2016) 1685–1699.

[61] M. Larriba, et al., Novel process to reduce benzene, thiophene, and pyrrole in gasoline based on [4bmpy][TCM] ionic liquid, Energy Fuels 32 (4) (2018) 5650–5658.

[62] P. Navarro, et al., Experimental screening towards developing ionic liquid-based extractive distillation in the dearomatization of refinery streams, Sep. Purif. Technol. 201 (2018) 268–275.