NEW SOLVENT SYSTEMS FOR DISTILLATION AND ABSORPTION INTENSIFICATION

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Abstract

Solvents with an improved price/performance ratio allow for processes with less operating and/or capital expenditure. Therefore, from an industrial perspective, it is worth reviewing the R&D progress in designing new competitive solvents on a regular basis. This paper aims at discussing the potential of new solvent systems applicable as absorbents or entrainers for boosting the performance of absorption and distillation processes. In this context, special focus will be dedicated to solvents like ionic liquids, amines and hyperbranched polymers. In particular, it will be demonstrated how these solvents can contribute to improve the performance of absorption processes such as absorption chillers and CO_2 capture processes as well as distillation processes like the separation of azeotropic mixtures by extractive distillation.

To illustrate the potential value of new solvent systems for the distillation and absorption community, the use of ionic liquids for absorption chillers is worth mentioning here. These sorption systems transform latent heat of the phase change liquid-vapor between different temperature levels by means of two working fluids, the refrigerant and the absorbent (working pair). The systems find use in different areas of application such as chiller applications (gas cooling, solar cooling, waste heat cooling), refrigeration, heat pumping and industrial heat recovery. One of the most prominent areas in which these absorption systems are applied is providing chilled water for air-conditioning by H_2O/LiBr absorption chillers. In this context, the development has led from single-effect to double-effect systems and from steam-fired to direct-fired generators. The main freedom in designing and improving these kinds of absorption processes lies in the choice of the working pair and in the principle of multistaging. Thus, a crucial fraction of fixed and/or variable costs for absorption chillers are defined by absorbent and refrigerant properties. Although many innovative working pairs have been suggested over the last decades, only two meet the prevailing industrial requirements: (a) H_2O/LiBr for water chillers and (b) NH_3/H_2O for refrigeration. However, these state-of-the-art working pairs show a number of drawbacks, including corrosiveness, a restricted temperature lift due to crystallization (H_2O/LiBr), toxicity, high working pressure and/or the need for rectification (NH_3/H_2O). Especially for multi-effect cycles with their potential for primary energy savings, selected ionic liquid-based absorbents combining a high capacity with adequate solution viscosities, thermal and chemical stability and a moderate corrosiveness at high process temperatures can substantially contribute to improve the performance of absorption chillers. This example indicates the potential of new solvents and underlines why this contribution will be dedicated to new solvent systems for distillation and absorption intensification. Apart from the use of suitable ionic liquids in absorption chillers, new solvent systems for carbon dioxide capture and extractive distillation will be presented and discussed from an industry perspective.

Keywords: absorption chiller, carbon capture, energy efficiency, ionic liquids, hyperbranched polymers.

1. Introduction

Ionic liquids[1,2] are most commonly defined as substances composed entirely of ions with melting points below 100 °C. More specifically, ionic liquids are organic salts that are fluid at (or close to) ambient temperature. Being a laboratory curiosity just a decade ago, ionic liquids are now available on large scale and some industrial applications are in the early stages of commercialization. Several more uses are currently being discussed and developed and much work remains to fully uncover the large potential of this novel class of liquids[57]. Their scientific and technical appeal is predominantly based on their variability and versatility. By selecting a suitable combination of cation and anion, the properties of ionic liquids can be adjusted over a relatively wide range. Among the most interesting and characteristic properties of ionic liquids are their extremely low volatility, their high thermal and electrochemical stability, their wide liquid ranges, the high dissolution power for a large variety of organic, inorganic and organometallic compounds, and the adjustability of their polarity as a function of different variables, e.g. composition[3-8]. While a lot of effort in past years has been put into obtaining pure compounds consisting of only one cation and one anion, it has become more evident recently that binary, ternary and higher mixtures of ionic liquids might be advantageous for finding suitable compositions in applications[57]. Furthermore, ionic liquids might have many advantages and might open new possibilities even when used in mixtures with other chemicals or materials. In fact, while early focus was put on developing ionic liquids as solvents for synthesis, the perception that ionic liquids are limited to replacing organic solvents in synthesis has changed as it has been shown that they can be employed as process aids, e.g. in the hydrosilylation of olefins (immobilization of otherwise homogeneous catalysts) and in the specific absorption of gases. Furthermore, due to their unique properties, ionic liquids create many interesting possibilities as far apart as performance additives and functional fluids in various materials and applications[57].

Based on these qualities, the consideration of ionic liquids in the search for improved chiller absorbents, e.g. for the replacement of LiBr, appears rather self-evident. In the Green Chemistry and Green Engineering context the use of ionic liquids as new absorbents in absorption chillers is of great potential relevance. This is due to the fact that the heat pump / absorption chiller technology is able to make use of so far un-used, low-temperature heat streams that are wasted today as their transformation to electrical energy is not efficient enough. Estimations for the European chemical industry alone calculate the amount of these waste heat streams to several hundreds of gigawatt hours per year. These waste heat streams can be converted by absorption chillers and/or heat pumps to provide either cooling or to be transformed to a higher temperature level[9]. To realize this enormous potential for energy savings and thus CO_2 emission reductions, more efficient absorption chiller technologies and heat storage technologies are required[57].

Ionic liquids are highly interesting absorbents for absorption chillers. In the following, the requirements and challenges for the use of ionic liquids in absorption chillers are discussed. After presenting a brief state-of-the-art summary, the progress in the development of ionic liquids as potential absorbents for refrigerants such as water is reported.

Absorption Chillers

As described by Ziegler, sorption systems such as used for chiller applications, refrigeration, and industrial waste heat recovery, transform latent heat of the phase change liquid/vapor or solid/vapor between different temperature levels[9]. Absorption chillers use two different working fluids, the refrigerant and the absorbent. In Figure 1, a basic absorption chiller cycle is illustrated. The four most important components are the evaporator E, where cooling is provided, the generator G, where the driving heat is conveyed to, and the absorber A and condenser C, from which the pumped heat is disposed off. In the generator, vapor is desorbed from the solution because of the heat input. The vapor is condensed, throttled and evaporated as in compression systems. After evaporation, the vapor is absorbed in the solution which is cooled in the absorber. The solution is pumped to the generator to be regenerated and throttled back to the absorber. To improve the efficiency, a solution heat exchanger SHX is introduced into the solution circuit. For cooling applications, the efficiency (Coefficient of Performance, COP) is defined as the ratio of cooling output, Q_0, to driving heat input, Q_2[9].
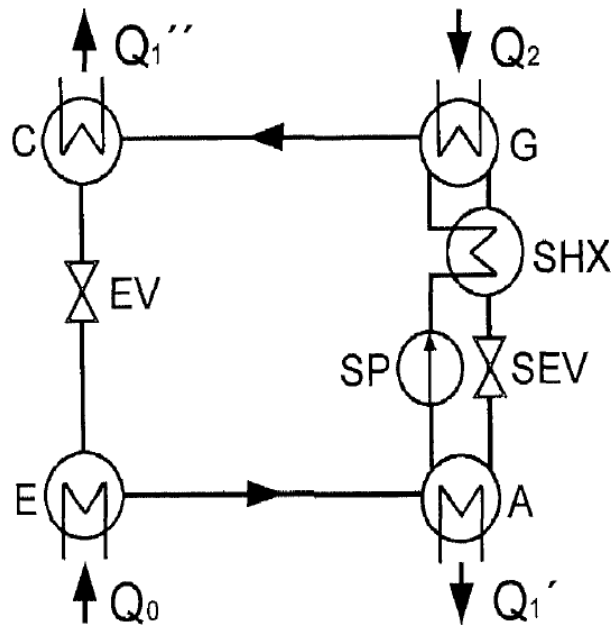
Figure 1. Flow sheet of a single-effect absorption chiller[9].
A: absorber; C: condenser; E: evaporator; EV: expansion valve; G: generator;
SEV: solution expansion valve; SHX: solution heat exchanger; SP: solution pump..

Absorption chillers are generally classified as direct- or indirect-fired, and as single, double - or triple-effect absorption chillers. In direct-fired units, the heat source can be gas or some other fuel that is burned in the unit. Indirect-fired units use steam or some other transfer fluid that brings in heat from a separate source, such as a boiler or heat recovered from an industrial process. Hybrid systems, which are relatively common with absorption chillers, combine gas systems and electric systems for load optimization and flexibility[55].

The main freedom in designing absorption systems lies in the choice of the working pair and in the principle of multi-staging. Thus, a crucial fraction of fixed and variable costs for absorption processes is defined by absorbent and refrigerant properties. Although many innovative working pairs have been suggested over the last decades[9], only two meet the prevailing industrial requirements:

(a) H_2O / LiBr for water chillers
(b) NH_3 / H_2O for refrigeration.

However, these state of the art working pairs show a number of drawbacks, including corrosiveness, a restricted temperature lift due to crystallization (H_2O / LiBr), toxicity, high working pressure and the need for rectification (NH_3 / H_2O). Especially for multi-effect cycles with their potential for primary energy savings, absorbents combining a high selectivity and capacity with thermal and chemical stability and a moderate corrosiveness at high process temperatures could lead to new industrial applications. This article focuses on the H_2O/LiBr-driven absorption chiller and the replacement of the LiBr absorbent by suitable ionic liquids.

2. Requirements and challenges[57]
When analyzing the state of the art concerning the potential use of ionic liquid-absorbents (see below) it becomes obvious that most of the requirements for using ionic liquids in absorption chillers are either not evaluated at all or not evaluated sufficiently. Therefore, in this section, the most important ionic liquid-requirements are presented.

In order to consider an ionic liquid as a genuine candidate for the utilization in an absorption chiller, several prerequisites have to be met. First and foremost, water should be well soluble in the ionic liquid without any liquid-liquid miscibility gap or crystallization border (thermodynamics). Secondly, the

15

ionic liquid should be hygroscopic and absorb water with an adequate capacity. Thirdly, the heat and mass transfer in the absorber, the generator and the heat exchangers is essential. Moreover, the ionic liquid should wet the surface of the heat exchanging areas in the chiller well over the relevant concentration levels and retain a low viscosity at both low water content and low system temperatures. Furthermore, the ionic liquids should not be corrosive and need to be compatible with standard chiller materials. A high long-term thermal and chemical stability is required, especially when considering double and triple effect chillers.

2.1 Thermodynamics, Heat and Mass Transfer

Apart from meeting essential heat and mass transfer requirements[9], the ionic liquid / refrigerant phase behavior is one of the most important aspects when evaluating the suitability of ionic liquids for chiller applications. Complete miscibility, the absence of crystal formation under operating conditions, and a decrease in the partial pressure of water (P_{H2O}) of comparable magnitude as for LiBr are crucial for optimizing the coefficient of performance. In case of ionic liquid absorbents, decreasing the partial pressure of the refrigerant is driven by the anion / cation combination. Especially with respect to water, a small activity coefficient γ_{H2O} mainly depends on the nature of the anion[23,54]. Further details are discussed below.

2.2 Crystallization behavior

Ionic liquids are characterized by a rather complex crystallization behavior. In fact, the existence of room temperature ionic liquids is a result of their inherent difficulty to crystallize. In many cases, the crystallization process is kinetically inhibited, so that super-cooling can be observed over extended periods of time (up to weeks). Measurements should therefore be checked carefully by DSC analyses before reporting a melting point. Sometimes, pour points offer good indications for the behavior under operating conditions. Furthermore, some ionic liquids completely lack a melting point, but show a glass transition temperature instead[26].

The melting point is a function of the substitution pattern and symmetry on the cation and the choice of the anion[56]. For any given anion, the melting point of the ionic liquid decreases with increasing linear alkyl chain length before reaching a minimum usually between six and eight carbon atoms[27]. The observation can be explained by a decrease of the effective colombic force between the ions and an impediment of efficient crystal packing. For longer chain lengths, the intermolecular van der Waals forces increase in relevance and lead to higher melting points. Liquid crystalline compounds can be obtained with chain length above 14 carbon atoms.

Not surprisingly, any branching of the alkyl chains or the introduction of functional groups which can form hydrogen bonds raises the melting point. For any given cation, the melting point very strongly depends on the anion. As might be expected, increasing electron delocalization in the anion lowers the melting point. For example, the melting point of [C2mim]Cl is reported at 87 °C, while the corresponding dicyanamide salt melts at less than 21 °C[28].

2.3 Corrosion behavior

The corrosion behavior of pure ionic liquids against different metals and alloys is currently under intense investigation (see also Chapter 4.3 of this book)[29,56]. The anion plays a prominent role in the corrosion process and therefore predominantly determines the corrosiveness of the compound towards ferrous metals. In case of non-ferrous metals, the complexation ability of both anion and the cation has to be considered. As far as the anions are concerned, halides are known to be problematic and should be avoided. Furthermore, halide impurities are commonplace due to current synthetic processes and possible contamination should be taken into account. At elevated temperatures, decomposition processes can liberate species that are more aggressive towards the metal or alloy. Generally, corrosiveness of ionic liquids towards ferrous metals is less problematic than towards non-ferrous metals.

2.4 Viscosity

The correct determination of the viscosities of pure ionic liquids is challenging because the viscosity is very sensitive towards even small amounts of contaminants. However, some general observations are worth reporting. Viscosities of ionic liquids vary over a large range[27,56]. Many ionic liquids behave more like honey at room temperature and there is really no upper limit. However, the lowest reported viscosities are in the range of ethylene glycol and therefore considerably higher than water or some conventional organic solvents. Importantly, the viscosities are very strongly temperature dependent

and even ionic liquids that are highly viscous at room temperature become easy to handle at moderately elevated temperatures well below their thermal decomposition[30]. The temperature dependence is less pronounced for low viscous ionic liquids posing a limit for attainable viscosities even at high temperatures.

As far as the selection of cations and anions is concerned, the main criteria to obtain lower viscosities are the size and the delocalization of the ions which limit their attractive intramolecular forces. Interestingly, functionalization in the side chain can be an important factor. Ether, hydroxyethyl and nitrile groups often reduce the viscosity significantly compared to their non-derivatized analogues of similar size[31].

2.5 Thermal Stability

The issue of thermal stability has been discussed controversially in the literature mainly due the application of different methodologies and the interpretation of data[32]. Most commonly, degradation temperatures are derived from the weight loss measured during fast scan thermogravimetric analysis (TGA) and / or differential thermal analysis (DTA). The correlation is justifiable due to the very low volatility of ionic liquids below the degradation temperature. However, even though the analytical methods are cheap, easily reproducible, and deliver data that are generally comparable, reported values for thermal stability vary widely. Therefore, it is important to look beyond the reported Ton-set values and consider the key parameters and assumptions under which the values were obtained. Important parameters are the rate of heating, the purity of the compound, the atmosphere and the material of the pan in which the compound is heated. But even the determination of Ton-set value from the measurement is open to interpretation. Some report Ton-set as the on-set point of weight loss, some report it after 5 % weight loss, some others use the step tangent method or the minimum in DTA curve method. These methods, however, reveal only the short term thermal stability and sometimes severely overestimate the maximum operating temperatures[33-35]. Therefore these values should be used for comparison relative to other compounds. Another useful method to obtain on-set temperatures of degradation is gas chromatography[36]. When employing ionic liquids as the stationary phase, the detection of the phase bleeding provides excellent comparative data[37].

The results published in the literature reveal several noteworthy general rules for the thermal stability of ionic liquids. The decomposition temperature depends very strongly on the nucleophilicity of the anion[38,39,26,56,57] because one of the main degradation pathways is the nucleophilic attack of the anion on the cation. Among the cations, phosphonium salts are the most stable, followed by imidazolium salts and ammonium salts. The thermal stability of imidazolium and similar cations can be improved by increasing the linear, short chain alkyl substitution on the ring. Also, it is well documented that halide-based anions exhibit poor thermal stability while anions with fluorinated alkyl chains show the highest reported decomposition temperature[27,56]. Further valuable results on the physicochemical and thermophysical properties of ionic liquids can be found elsewhere[44-55,57].

3. State-of-the-art and selected results

Several research groups studied the phase behavior of ionic liquid / water systems[10-21,54,57]. In this context, a wide variety of ionic liquids has been investigated such as $[C_2mim][PF_6]$, $[C_4mim][PF_6]$, $[C_8mim][PF_6]$, $[C_4mim][BF_4]$, $[C_8mim][BF_4]$, $[C_4mim]Cl$, $[C_2mim][Tf_2N]$, $[C_4mim][Tf_2N]$, $[C_1mim][DMP]$, $[C_4mim]Br$, $[C_2OHmim][BF_4]$, $[C_4mim]I$, $[C_2mim][diethylphosphate]$, $[C_4mim][dibutylphosphate]$.

In addition, other potential ionic liquid / refrigerant systems have been studied: Cai *et al.* developed a dynamic model for a single-effect absorption chiller cycle using ionic liquids as absorbent. Thermodynamic properties were obtained from an equation of state for the refrigerant/absorbent mixtures. The COP of a system using CO_2 / $[C_4mim][PF_6]$ was much lower than that of a traditional system using NH_3 / H_2O but questions remain regarding the accuracy of the thermodynamic approach chosen. Some design and operation parameters that affect the cycle performance were identified and the transient response of the cycle was investigated[17].

Kim *et al.* investigated $[C_4mim]Br$ / trifluoroethanol and $[C_4mim][BF_4]$ / trifluoroethanol as potential working pairs for absorption heat pumps. Refractive indices and heat capacities were determined in the temperature range of 298.2 – 323.2 K. The partial pressure of trifluoroethanol (TFE) was measured using the boiling point method in the concentration range of 40.0 – 90.0 wt% of ionic liquid

and were successfully correlated with an Antoine-type correlation. The partial pressure results indicate that the absorption performance of [C₄mim]Br is better than for the ionic liquid [C₄mim][BF₄][18].

Ionic liquid/CO_2-working pairs such as [C₄mim][PF₆] / CO_2 combination to be used for absorption refrigeration have been proposed by Sen and Paolucci. Based on a promising absorption performance and a good thermal stability the authors concluded that the ionic liquid proposed represent a suitable absorbent for absorption refrigeration. Key properties defining the ideal ionic liquid for absorption refrigeration systems were discussed as well. However, it was noted that most thermodynamic and thermophysical ionic liquid-properties, that are required to discuss the ionic liquid-potential for absorption refrigeration, are not available in literature[19].

Yokozeki and Shiflett determined solubilities of ammonia in [C₂mim][acetate], [C₂mim][SCN], [C₂mim][C₂H₅SO₄], [dimethylethylammonium][acetate] at isothermal conditions between 283 and 373 K and in a concentration range between 30 and 85 mol% of ammonia. For the investigated ionic liquid, very high NH_3 solubilities were found. The pressure-temperature data obtained were successfully described using an equation of state. All the excess properties showed negative values, reflecting strong intermolecular complex formation. The authors concluded that the ionic liquid/NH_3-systems investigated represent promising working pairs for the field of absorption refrigeration[21,21,57].

In Figure 2, vapor-liquid equilibria (VLE) of different ionic liquid/water-systems are depicted at T = 35 °C. The ionic liquids used are commercially available from Evonik Degussa. The VLE measurements were carried out according to the procedure described by Evonik Degussa[11,12,40]. Unlike LiBr, at T = 35 °C, no crystal formation occurs over the entire concentration range. The ionic liquids investigated have alkylimidazolium cations. As demonstrated elsewhere, the cation has a negligible influence on the partial pressure of water[3,23,53,57]. However, the choice of the anion is essential when aiming at lowering P_{H2O}. While the ethylsulfate anion of Tego ionic liquid IMES ([C₂mim][C₂H₅SO₄]) corresponds to a moderate decrease of P_{H2O}, the dimethylphosphate anion of the ionic liquid [C₁mim][dimethylphosphate] leads to a stronger attraction of the water molecules corresponding to a smaller activity coefficient γ_{H2O}. However, with increasing compactness of the anion, the partial pressure can be decreased further. This becomes obvious for [C₂mim][acetate], an ionic liquid that even allows reaching the minimum pressure of the LiBr / H_2O system at high ionic liquid concentration. Therefore, the absorption performance for alkyl-imidazolium-based ionic liquids improves with increasing compactness of the anion according to our preliminary conclusions, *i.e.* γ_{H2O} ([acetate]⁻) < γ_{H2O} ([dimethylphosphate(DMP)]⁻) < γ_{H2O} ([ethylsulfate]⁻).
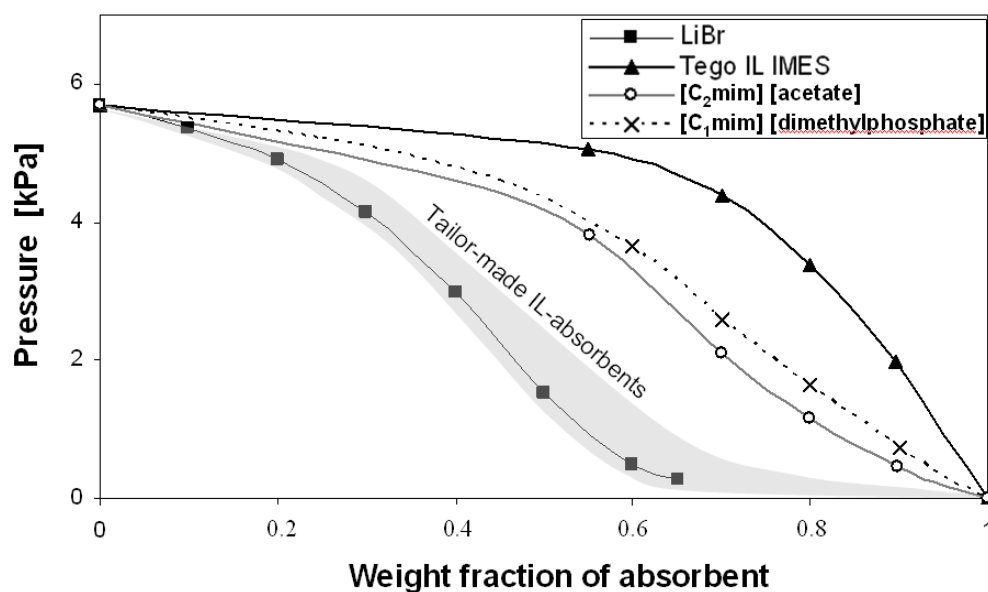
Figure 2. Experimental VLE results for selected ionic liquid / water systems at T = 308.15 K.

Based on these results, Evonik Degussa currently synthesizes and evaluates tailor-made ionic liquid-absorbents. The absorption performance of the latter candidates is indicated by the grey shaded area that is highlighted in Figure 2. In addition, adjusting the property profile of an ionic liquid-based working pair to the aforementioned requirements by the use of high performance additives can help leveraging the full potential of ionic liquids in this field. Further state-of-the-art information on the potential use of ionic liquids in absorptions chillers can be found elsewhere[22-25,54,57].

Apart from the use of suitable ionic liquids in absorption chillers, new solvent systems for carbon dioxide capture and extractive distillation will be presented and discussed from an industry perspective.

Nomenclature / Abbreviations

P_{H2O} Partial pressure of water, kPa
VLE   Vapor-liquid equilibrium
TFE   Trifluoroethanol
COP   Coefficient of Performance

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