Thermodynamics and economics of liquid desiccants for heating, ventilation and air-conditioning – An overview

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Abstract

In an effort to minimise electricity consumption and greenhouse gases emissions, the heating, ventilation and air-conditioning sector has focused its attention on developing alternative solutions to electrically-driven vapour-compression cooling. Liquid desiccant air-conditioning systems represent an energy-efficient and more environmentally friendly alternative technology for dehumidification and cooling, particularly in those cases with high latent loads to maintain indoor air quality and comfort conditions. This technology is considered particularly efficient in hot and humid climates. As a matter of fact, the choice of the desiccant solution influences the overall performance of the system. The current paper reviews the working principle of liquid desiccant systems, focusing on the thermodynamic properties of the desiccant solutions and describes an evaluation of the reference thermodynamic properties of different desiccant solutions to identify which thermodynamic, physical, transport property influences the liquid desiccant process and to what extent. The comparison of these thermodynamic properties for the commonly used desiccants is conducted to estimate which fluid could perform most favourably in the system. The economic factors and the effect of different applications and climatic conditions on the system performance are also described. The paper is intended to be the first step in the evaluation of alternative desiccant fluids able to overcome the problems related to the use of the common desiccant

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solutions, such as crystallization and corrosion to metals. Ionic liquids seem a promising alternative working fluid in liquid desiccant air-conditioning systems and their characteristics and cost are discussed.

Keywords: Liquid desiccant; moisture removal; thermo-physical properties; thermo-chemical energy storage; economic factor; ionic liquids;

Nomenclature	
a_P	wetted surface area of packing [m^2/m^3]
a_w	water activity [-]
c_p	specific heat capacity [kJ/(kg °C)]
D	diffusion coefficient [m^2/s]
d_{eq}	equivalent diameter of packing [m]
d_p	normal diameter of packing [m]
F	superficial flow rate [kg/(m^2 s)]
Δh_{abs}	heat of absorption [kJ/kg]
h_h	heat transfer coefficient [W/(m^2 °C)]
h_m	mass transfer coefficient [kg/(m^2 s)]
k	thermal conductivity [W/(m °C)]
Le	Lewis number [-]
m	mass flow rate [kg/s]
Nu	Nusselt number [-]
NTU	number of mass transfer units [-]
P	pressure [kPa]
Pr	Prandtl number [-]
R	universal gas constant [kJ/(mol °C)]
RH	relative humidity [-]

Re	Reynolds number [-]
T	temperature [°C]
Sc	Schmidt number [-]
Sh	Sherwood number [-]
x	mass fraction of desiccant solution [kg $_{solute}$/kg $_{solution}$]
y	molar fraction of desiccant solution [kmol $_{solute}$/kmol $_{solution}$]

Greeks symbols

γ	activity coefficient [-]
μ	chemical potential [J/kg]
ρ	density [kg/m^3]
v	dynamic viscosity [mPa s]
λ	latent heat of vaporization [kJ/kg]
ω	moisture content [kg $_{H2O}$/kg $_{dry\ air}$]
ω_{equ}	equilibrium moisture content [kg $_{H20}$/kg $_{dry\ air}$]
Φ	osmotic pressure [Pa]
σ	surface tension [N/m]

Subscripts

a	air
conc	concentrated solution
dil	diluted solution
g	gas phase
in	inlet
l	liquid phase
out	outlet
sol	desiccant solution

w, s	saturated water vapour
w	water
Abbreviations	
CaCl$_2$	calcium chloride
Ca(NO$_3$)$_2$	calcium nitrate
CHP	combined heat and power
e-NRTL	electrolyte non-random two liquid model
ERH	equilibrium relative humidity
HCO$_2$K	potassium formate
MgCl$_2$	magnesium chloride
IL	ionic liquid
LiBr	lithium bromide
LiCl	lithium chloride
LDAC	liquid desiccant air-conditioning
NH$_4$NO$_3$	ammonium nitrate
TEG	tri-ethylene glycol
[BMIM][BF$_4$]	1-butyl-3-methylimidazolium tetrafluoroborate
[DMIM][OAc]	1,3-dimethylimidazolium acetate
[DMIM][BF$_4$]	1,3-dimethylimidazolium tetrafluoroborate
[EMIM][OAc]	1-ethyl-3-methylimidazolium acetate

1. Introduction

Due to rapid population growth and the higher standards of human living, the electric consumption for the heating, ventilation and air-conditioning (HVAC) sector and the resulting HVAC equipment demand has reached record levels, as displayed in Figure 1 [1]. This increase of the energy consumed for the HVAC results in higher fossil fuel consumption, increase in peak electric demand, straining the electricity grid at

peak times [2]. As shown in the Figure, the trend of the equipment demand for the HVAC sector is significantly increased in last years, reaching a 6.2 % growth in the period 2009-2014, while the energy consumption for air-conditioning in the non-residential building sector accounts between 20 and 60% [3].
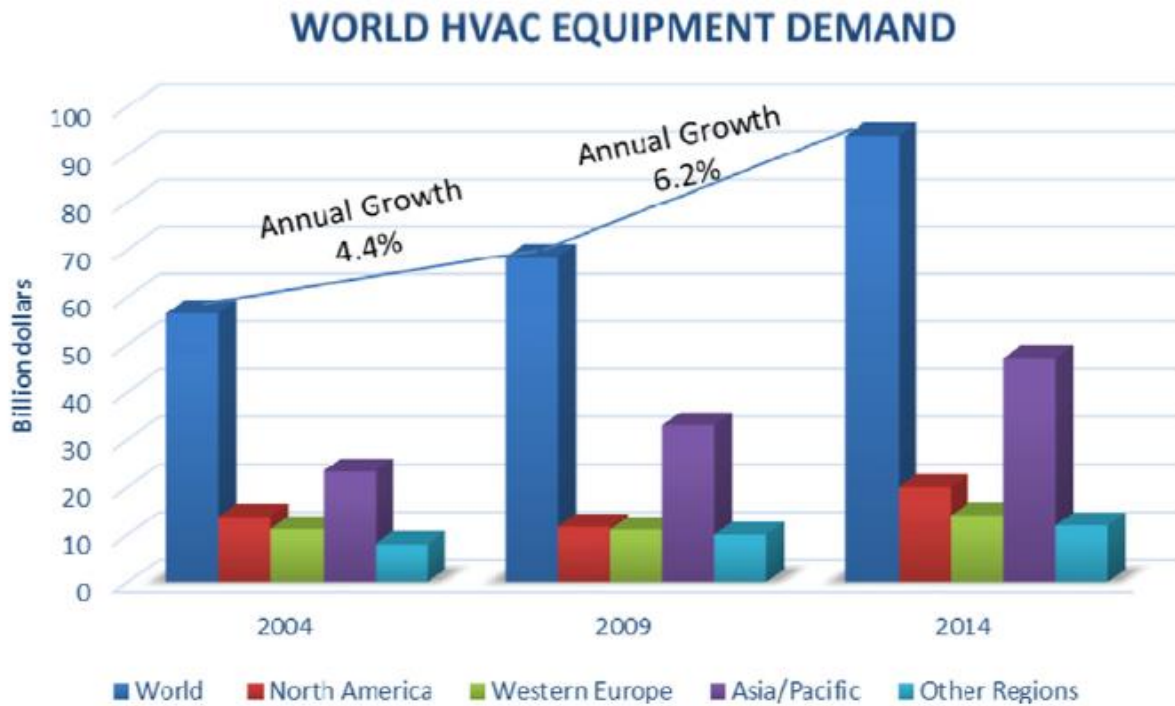
WORLD HVAC EQUIPMENT DEMAND

Figure 1 Overall HVAC equipment demand and trend [1].

In the design of HVAC systems, it should be carefully evaluated the quantity of moisture present in the ventilation air, which could be responsible for structural problems to the building and comfort and health problems for the occupants. The sources of the moisture in a building are permeation through floors, walls and ceiling, evaporation from occupants' clothing, breath and perspiration, air infiltration through leaks, holes and door openings, and outside air ventilation [4]. Ventilation air is the most responsible for the moisture load in different applicative sectors [4]. These moisture in the air contributes to the latent load in the HVAC system. As reported by [2] and [5], latent loads are always higher than sensible loads, except for desert climates. The high latent load could result in an inefficient dehumidification process with

conventional vapour-compression systems [6]. Due to the development of ASHRAE standards 62 [7] and 90 [8], the conventional vapour-compression systems have progressively become less efficient in dealing with latent loads present in buildings, causing an oversize of the system when it must deal with high moisture content [2]. An oversized system results also in an increase of the capital cost of the system of the ductwork installation and of the operating cost for fans. In addition to that, an ulterior issue in conventional air-conditioning systems is the re-evaporation in the building of the moisture condensed when the coil is off, resulting in dehumidification inefficiency when the system is switched on/off [9]. To conclude with, conventional vapour-compression systems have a poor control capacity, being not able to efficiently deal with changes in sensible and latent loads [3].

For these reasons, concerns related to the sustainability and efficient use of available energy resources without threatening the world's future has led to intensive research programs targeting energy-efficient and environmentally friendly HVAC technologies, particularly in the development of system able to efficiently deal with the moisture. Liquid desiccant air-conditioning (LDAC) represents one of the promising alternative technology for efficient de/humidification and heating/cooling, able to be driven by the heat coming from excess (or waste) low-temperature renewable energy sources such as those from power plants or industrial processes. The utilisation of heat to drive its process rather than electricity consumption of conventional vapour-compression HVAC systems results in significant electric and economic savings and from an environmental viewpoint, resulting in lower CO_2 emissions. In addition to that, LDAC technology uses working fluids not responsible for the ozone depletion, as CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons), and for the greenhouse effect, as HFCs (hydrofluorocarbons). The solutions used in LDAC systems have absorption/desorption properties for use with water vapour, are known as liquid desiccants [10-12]. Exploiting the hygroscopicity of these solutions, LDAC technology can dehumidify and cool the air for building and industrial applications.

The employment of hygroscopic liquid desiccant solutions for air-conditioning has been investigated in the past [13-18]. The most commonly employed liquid desiccant solutions are halide salts aqueous solutions, e.g. aqueous solutions of lithium chloride (LiCl), lithium bromide (LiBr), calcium chloride

(CaCl2), magnesium chloride (MgCl2), etc. and tri-ethylene glycol (TEG). The thermodynamic properties of these liquid desiccants have been determined and reported in detail [19-22]. Meanwhile, the employment of alternative solutions as desiccant to overcome the drawbacks of these common desiccant solutions have also been investigated [23-27].

The thermodynamic properties of the liquid desiccants play a fundamental role in the overall economic and operational performance of LDAC systems and require further on-going exploration and review. Therefore, the current paper is addressed to review which properties make a fluid best placed for use in an optimised liquid desiccant dehumidification processes and why. Moreover, an evaluation of the economic factors involved in LDAC process is performed. The paper is structured as follows. Section 2 gives a brief introduction of desiccants (solid and liquid), describing LDAC systems and the advantages resulting from the use of this technology. Section 3 evaluates the thermodynamic and transport properties involved in the liquid desiccant dehumidification process and that are fundamental in the choice of a fluid as desiccant. The analysis of liquid desiccants continues in Section 4 and 5 where the economic, applicative, and climatic factors involved in the process are described. To conclude with, Section 6 briefly illustrates advanced new fluids used as liquid desiccant, particularly focusing on the possibility of using ionic liquids in LDAC systems.

2. LDAC technology overview

2.1. Desiccants overview

Desiccants are substances with a high affinity to water vapour, able to dehumidify the air. Based on their physical state, these materials can be classified by their state, i.e. solid desiccant and liquid desiccant [15]. Both these desiccants have been widely used for dehumidification, cooling and drying purposes [28-30]. The moisture removal process of these desiccants is based on two different physical processes, namely adsorption and absorption. The physical difference between the two processes is illustrated in Figure 2.
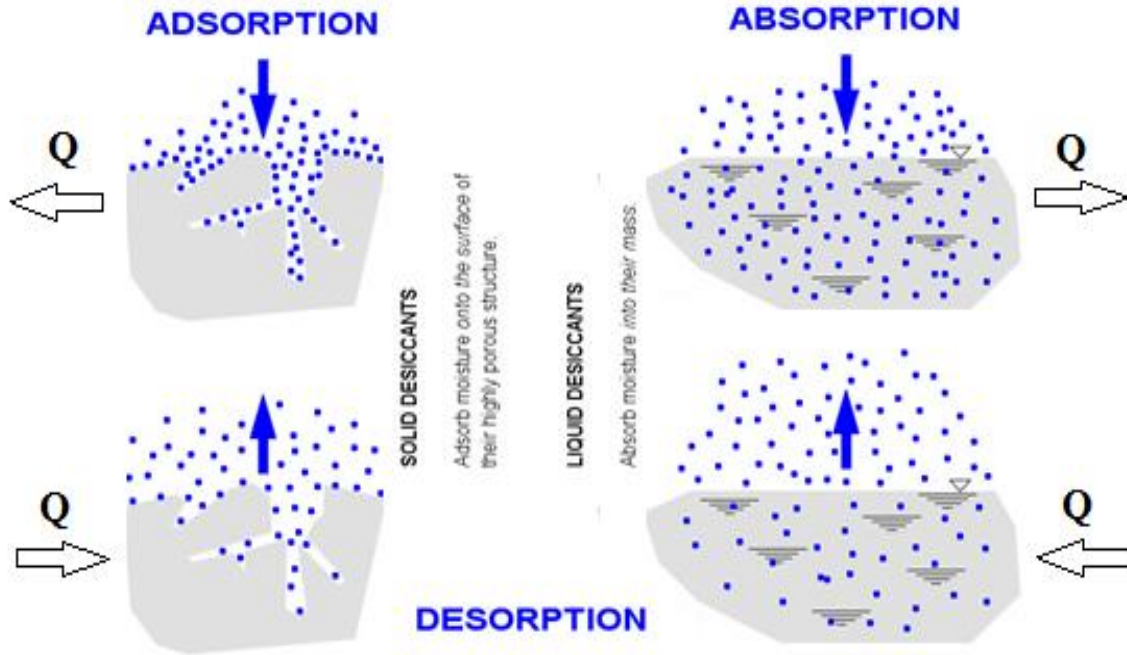
Figure 2 Comparison of adsorption and absorption process [31, modified].

The adsorption process, typical of solid desiccants, involves the physical entrapment of the water molecules inside the porous structure of the desiccant where the moisture is held. The most commonly employed solid desiccants are silica gels, zeolites, synthetic zeolites, activated alumina, carbons, and synthetic polymers [15]. On the other hand, the water molecules in the absorption process are included in the mass of the liquid desiccant solution. The process is driven by the vapour pressure difference between the surface of the liquid desiccant solution and the process air, therefore it is characterised by the complete integration of a substance into another [32]. However, the dehumidification for these two desiccants can be considered in some way similar because they are both exothermic reactions characterised by the transfer of condensation heat from the water vapour to the desiccant material.

The solid desiccant system requires relatively higher regeneration temperature comparing to liquid desiccant [33]. To physically move the desiccant to form a continuous dehumidification process, a rotating desiccant wheel is normally used as shown in Figure 3 [34]. The moisture adsorption/desorption process is continuous, therefore not presenting any opportunity for thermal energy recovery. The ideal

dehumidification process by solid desiccant is isenthalpic, therefore the removal of moisture in the air is accompanied by an increase in the air temperature that must be cooled after the dehumidification before being supplied to the zone to be conditioned.
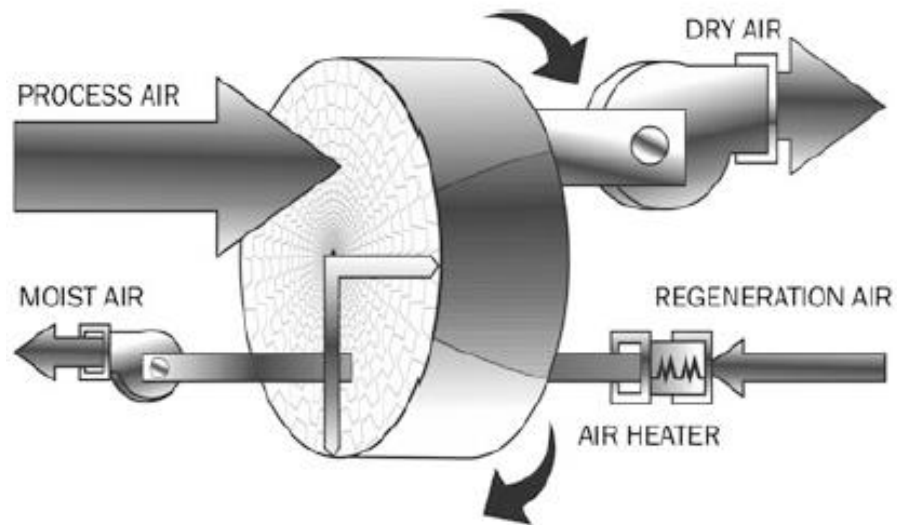

Figure 3 Example of solid desiccant wheel [34].

Whilst not as mature, the liquid desiccant technology is very promising for several aspects. Firstly, the liquid desiccant system has a greater scope to remove moisture compared to solid desiccant system and can simultaneously provide dehumidification and cooling under real-world working conditions [15, 28]. The fluid nature of liquid desiccant allows removing the latent heat released by the water vapour during the dehumidification process with a third fluid, usually water. This helps to keep the moisture absorption capacity constant during the dehumidification and to improve the dehumidification performance and sensible heat removal of the process.

2.2. LDAC overview

Even if less known than conventional vapour-compression cooling, the origins of liquid desiccant cooling can be found as earlier as vapour-compression technology. The first attempt to control temperature and humidity can be found at the beginning of the 20th century with Harris [35], which developed an air-conditioning system for an auditorium based on temperature reduction performed by ice and humidity control performed by $CaCl_2$. In 1935, Bichowsky and Kelley [36] developed the first system for air-conditioning comparable to the actual LDAC system. The system is represented in Figure 2, where the moisture removal ability of a LiCl solution is employed for air-conditioning.
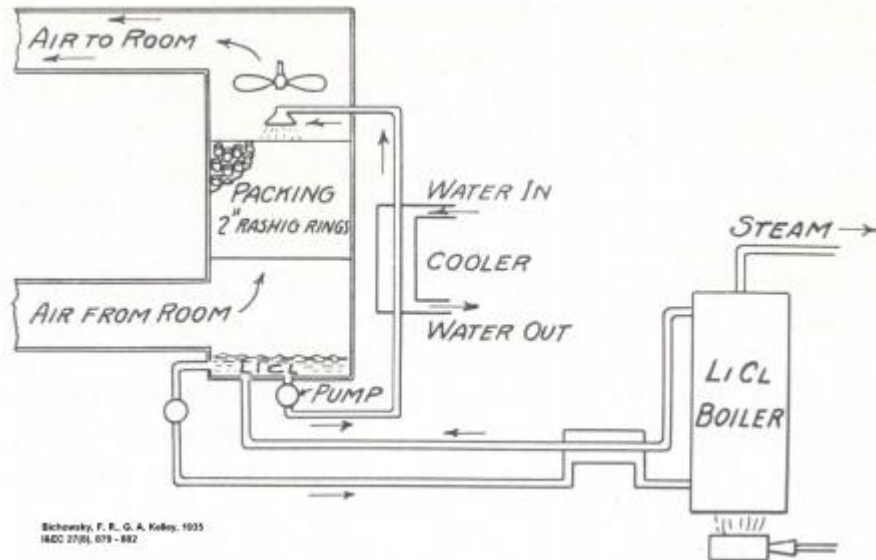

Figure 4 Schematics of the liquid desiccant system proposed by [36].

The first liquid desiccant air-conditioning system driven by solar energy was introduced by Lof in 1955 [4]. In the system, TEG solution was employed for an air dehumidification process driven by solar energy. Nevertheless, the decline of the electricity price in the 50's and 60's drove the worldwide development of vapour-compression air-conditioning systems and the contemporary abandonment of the liquid desiccant technology [37]. Following the Middle Eastern oil crisis of 1973 and 1979, a renewed interest in the more efficient use of the energy resources led the liquid desiccant system to start to be employed for air-

conditioning and not just for air dehydration in industrial processes [6, 38]. However, the insufficient maturity of liquid desiccant technology due to its drawbacks, such as corrosion, carry-over of liquid desiccant droplets, etc. have limited the worldwide employment in the past [39].

The common configuration of a LDAC system is shown in Figure 5. The main components are dehumidifier (absorber), humidifier (regenerator), solution heat exchanger, heating source, cooling source, pumps, and fans.

Figure 5 Configuration of a common LDAC system.

In the dehumidifier, a nozzle is used to spray the solution from the top and the solution comes into contact with the process air which is blown upwards from the base. The solution absorbs the water molecules from the air, providing a dehumidified stream for air-conditioning. The driving force of this absorption process is the low equilibrium vapour pressure of the desiccant solution (depicted in the figure as the strong solution) respect the partial vapour pressure of the water vapour in the outside air. The water vapour is attracted and absorbed by the desiccant solution, leading to the reduction of the moisture content in the processed air. The process continues until the solution reaches equilibrium with the

processed air. In the regenerator, the opposite process takes place, meaning that the high vapour pressure on the surface of the desiccant solution (here represented as the weak solution) causes the release of the water vapour to the scavenging air, humidifying it before usually dumping it to the environment. This process requires heat input because the solution must be at relatively high temperature (approximately in the temperature range between 55 °C and 70 °C) to have the high enough vapour pressure to desorb the water vapour to the air and re-concentrate the solution to be re-used in the dehumidifier [10]. On the other side, the solution demands to be cooled before entering the dehumidifier to reach the needed value of low equilibrium vapour pressure. This cooling demand depends on the solution properties, mass flow rate and the minimum temperature needed for the solution to desorb water [6]. The cooling is usually performed by a cooling tower/chilled water system. A solution heat exchanger is employed for the solution to be cyclically processed in the system. The heat exchanger is used to precool the strong solution before passing through the cooling system and to preheat the weak solution before the regenerative heat source. This heat exchanger involves only sensible heat exchange between the weak and strong solution and is used to improve the overall performance of the system due to the reduction of the heating and cooling load before the dehumidification and regeneration process. The fans and the pumps blow the air and pump the solution through the system, respectively. Only these two components are responsible for electricity consumption in a LDAC standalone system.

2.3. Energy use of liquid desiccant systems

The main capacity of LDAC systems is their ability in dealing with moisture removal. However, their ability to deal with sensible loads is fairly limited [40, 41]. For this reason, the integration of liquid desiccant systems with systems able to control the supply air temperature has been crucial for the worldwide marketability of liquid desiccant systems. In the past, the decoupling of latent and sensible cooling with the integration of liquid desiccant systems with vapour-compression system, absorption chillers or evaporative coolers has been largely investigated [42-49]. The combination of sensible cooling performed by vapour-compression chiller and latent cooling performed by liquid desiccant technology

results in a COP increase, due to the higher evaporation temperature reachable by the vapour-compression system [3]. Moreover, the condenser heat can be used in hybrid systems as heat input of the desiccant regeneration process [12]. The integration of direct evaporative coolers with LDAC systems has been proved as efficient in greenhouses [12]. However, the cooling obtained with direct evaporative coolers results in a humidity increase of the supply air. Therefore LDAC system must over dehumidify the supply air. For this reason, the integration of LDAC with indirect evaporative cooling has been considered as more promising.

The ability of the desiccant solution to dehumidify the process air decreases as it absorbs the moisture, increasing its temperature. This property will be more accurately described in the Section 3.1.1. Lowenstein et al. [42] developed a liquid desiccant system internally-cooled by a third fluid (water) to reduce the degradation of the dehumidification performance of the system. Woods and Kozubal [43] developed an enhanced internally-cooled dehumidifier integrated with an indirect evaporative cooler (DEVAP) to significantly increase the performance of the system. Respect the DEVAP that deals with a mix of outdoor and return air, the utilisation of a 100% outdoor air could produce favourable effects in terms of indoor air quality and productivity [44]. Jeong et al. [45] studied the replacement of Variable Air Volume (VAV) systems with a combination of Liquid Desiccant and Indirect and Direct Evaporative Cooling (LD-IDECOAS). The Indirect/Direct Evaporative Cooling assisted-100% Outdoor Air System has been proved as an energy-efficient replacement of VAV systems. However, this is not true in hot and humid climates, where the integration of the system with LDAC technology results highly performing. An improvement of the system has been obtained by using a dew-point evaporative cooler as sensible cooler [44, 46]. The performance of the overall system is highly increased by the replacement of the sensible cooler [12]. Jeong et al. [44] developed a Liquid Desiccant and Dew Point Evaporative Cooling-assisted 100% Outdoor Air system (LDEOS) able to replace the conventional vapour-compression system all year round under Korean climatic conditions.

One of the main advantages of the LD technology is the efficient use of relatively low-temperature heat, required by its process. This feature makes the technology very interesting with renewable energies, such

as geothermal [47] and solar energy, directly delivered from a solar collector/regenerator or indirectly from flat plate solar collectors, evacuated tube solar collectors, and parabolic solar collectors [12]. Moreover, the system could efficiently exploit heat from Combined Heat and Power (CHP) systems or district heat, and recover low-temperature industrial excess heat that would be otherwise be wasted [38]. Dong et al. [48] investigated the energy savings resulting from a DEVap system driven by district heat source. The simultaneous production of power, heating and cooling obtainable by the combination of liquid desiccant technology with CHP systems is one of the most promising, particularly for applications where the humidity removal is fundamental [41]. Recent studies also showed the feasibility of the coupling of fuel cells with liquid desiccant technology [40, 49]. Elmer [40] investigated the feasibility of using a Solid-Oxide Fuel Cell (SOFC) to produce electricity and drive the regeneration process of the liquid desiccant, while Kim et al. [49] investigated the integration of the liquid desiccant system with a Proton Exchange Membrane Fuel Cell (PEMFC). The efficiency of these fuel cells together with their thermal output makes them very promising for integration with liquid desiccant technology.

Another energy-related application of liquid desiccant solutions is their potential as thermo-chemical storage medium [50, 51]. This ability of liquid desiccant solutions will be more accurately described in Section 3.4.

2.4. Liquid desiccant characteristics

The overall performance of LDAC system is highly dependent on the different chemical and physical properties of the employed liquid desiccant. As previously mentioned, desiccant solutions are primarily used because of their hygroscopic properties, namely the strong affinity of the solution to the molecules of water vapour. However, this is not the only property affecting the dehumidification performance of the system. Other properties, such as density, dynamic viscosity, heat and mass transfer potential, thermal energy storage potential, also play a fundamental role in the system performance. The best desiccant in LDAC systems should lead to both of dehumidification/cooling performance improvement and economic

saving. Therefore, all the thermodynamic properties involved in LDAC process must be carefully evaluated.

The first solar liquid desiccant cooling system employing a tri-ethylene glycol (TEG) solution as working fluid was developed by Lof in 1955 [4]. TEG is an organic liquid compound characterised by hygroscopicity and the ability to dehydrate natural gas. The high viscosity and volatility of this solution created serious drawbacks to the system of stagnation and carry-over of the solution in the processed air and limited the utilisation of TEG in LDAC system [33]. However, TEG solution is still employed in dehumidification for industrial applications, where the occupants' health is not the primary issue. Metal halide salts (LiCl, LiBr, $CaCl_2$, $MgCl_2$, etc.) solutions have been identified to be able to overcome the drawbacks of glycols (TEG). These solutions have low equilibrium vapour pressure, which is a merit to ensure the dehumidification process. Apart from that, other thermodynamic properties, such as density, viscosity, etc., make the halide salts solutions the most common choice for LDAC systems. LiCl solution is the desiccant solution mostly used worldwide. The suggested reason for that is to be found in the lower cost of LiCl in the 1930s and the offensive odors sometimes produced by the other desiccant tested in the period (e.g. LiBr solution) [41].

Nevertheless, the aforementioned liquid desiccant solutions still present some thermo-physical and economic drawbacks and therefore do not represent the optimal solution employable in LDAC systems. In the recent period, the individuation of alternative solutions for LDAC systems has been evaluated [23-25]. Less-corrosive and non-volatile desiccants such as salts of weak organic acids of potassium and sodium, e.g. potassium formate (HCO_2K), potassium acetate (CH_3CO_2K), sodium formate (HCO_2Na) and sodium acetate (CH_3CO_2Na) were investigated in these systems [51, 52]. The characteristics of HCO_2K solutions of low crystallization temperature, low density and viscosity, high solubility, less corrosion to metals, and less toxicity make of this desiccant a very promising candidate for LDAC technology. Though the dehumidification ability of HCO_2K solution is weaker than the common desiccants, it still could dehumidify the air to about 30% RH [33]. Moreover, the cheaper price of this weak organic salt could lead to an important economic saving in the total system cost. Longo and Gasparella [53] showed

how HCO$_2$K solutions are interesting for humidity removal in technical applications, although they are less effective as desiccant of halide salt solutions.

The framework for the evaluation of a fluid as liquid desiccant is shown in Table 1. Following this framework, the thermo-physical and economic properties of the mostly used desiccants, e.g. LiCl, LiBr, CaCl$_2$, MgCl$_2$ and HCO$_2$K aqueous solutions, will be investigated in the next section.

Table 1 Framework for the evaluation of liquid desiccants.

Characteristics	Properties
Dehumidification ability	• Equilibrium vapour pressure and equilibrium moisture content
	• Water activity, activity coefficient, chemical potential, osmotic pressure
Thermo-physical properties	• Density
	• Viscosity
	• Specific heat capacity
	• Enthalpy of absorption, enthalpy of mixing
Heat and mass transfer	• Thermal diffusivity
	• Diffusion coefficient of water vapour in solution
	• Henry's law constant
	• Surface Tension
Other properties	• Thermo-chemical energy storage
	• Health and safety requirements
	• Corrosion to metals
	• Economics
	• Application and climatic conditions

3. Thermodynamic properties of liquid desiccants

3.1 Moisture absorption/desorption ability

The hygroscopicity of a desiccant solution is evaluated through several properties, including equilibrium vapour pressure, equilibrium moisture content and relative humidity, water activity and colligative properties.

3.1.1 Equilibrium vapour pressure and crystallization control

The equilibrium vapour pressure, namely the pressure of the water molecules on the solution surface in equilibrium with the molecules of water vapour present in the surrounding air, is the primary factor in the determination of the dehumidification ability of a hygroscopic desiccant solution. When a hygroscopic substance is dissolved into water, the equilibrium vapour pressure at the liquid-air interface is lower than the vapour pressure of pure water. In the absorber/dehumidifier, the driving force of the absorption process is the pressure difference between the low water vapour pressure of the liquid desiccant and that of the humid air. The lower the equilibrium vapour pressure of the solution, the more effectively the liquid desiccant solution will be able to absorb the water vapour from the process air. A solution with a lower equilibrium vapour pressure will hence be able to dry humid air to lower relative humidity.

The equilibrium vapour pressure of a solution is a thermodynamic function depending on temperature, concentration of the solute and pressure. For open systems (e.g. at ambient pressure), the lower equilibrium vapour pressure, i.e. better dehumidification ability, is reached for higher concentrations and lower temperatures. Unfortunately, there are no current analytical models for the evaluation of the vapour pressure of different solutions. Most of the property calculations are based on the fitted correlations on experimental results [19, 20, 22]. In this paper, an empirical correlation, the Cisternas-Lam equation [54], was used for the evaluation of the moisture absorption capacity of different desiccant solutions. This model is able to calculate equilibrium vapour pressure of several electrolyte solutions. Although not particularly accurate at higher concentrations and temperatures, this empirical correlation can be helpful for the evaluation of which electrolyte solution could be potentially used as desiccant. In Figure 6, the

equilibrium vapour pressure based on the Cisternas-Lam model of different desiccant solutions are shown, including the common used LiCl, LiBr, CaCl₂, MgCl₂ solutions and alternative desiccants calcium nitrate (Ca(NO₃)₂) and ammonium nitrate (NH₄NO₃) solutions. These two alternative desiccants have been investigated due to their less corrosion because not composed by chlorine or bromide ion. All equilibrium vapour pressures of different desiccants are calculated based on the saturated concentration at 25 °C considering a dehumidification situation.
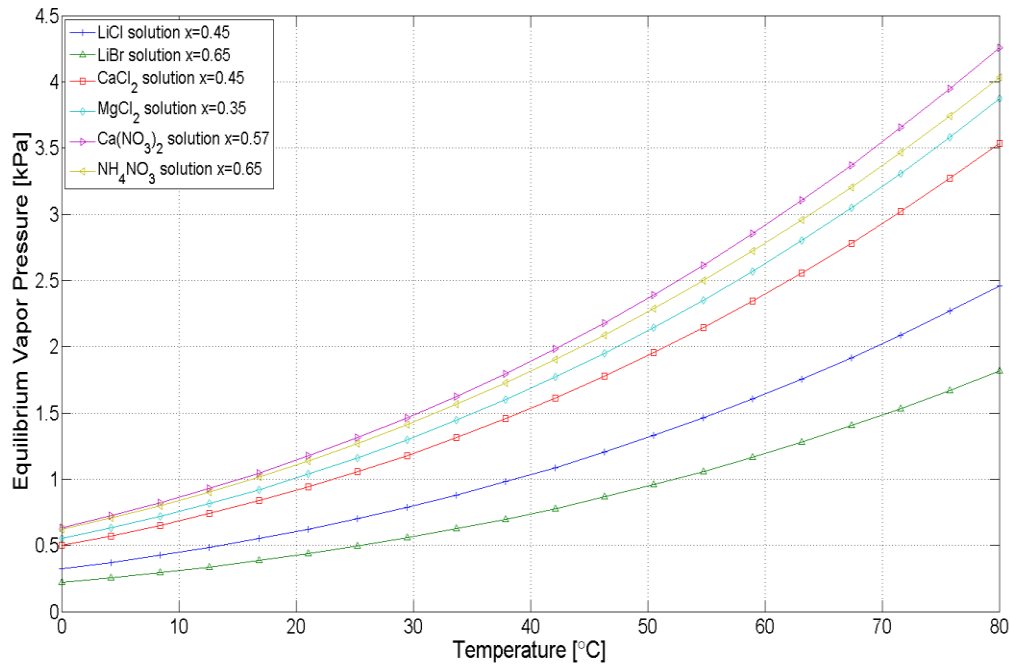
Figure 6 Equilibrium vapour pressure of liquid desiccants based on Cisternas-Lam model.

As shown in Figure 6, LiBr and LiCl solutions have the lowest equilibrium vapour pressure, i.e. highest dehumidification ability, followed by CaCl₂ and MgCl₂ solutions. The Cisternas-Lam model is not particularly reliable for the calculation of the equilibrium vapour pressure at higher values of concentration and temperature [32] and as such will not be used again for the equilibrium vapor pressure evaluation of liquid desiccants. As aforementioned, the most interesting liquid desiccants for HVAC application are LiBr and LiCl for their higher dehumidification performance, CaCl₂ for its lower cost, and

HCO₂K for its lower corrosion to metals and crystallization. Therefore in Figure 7, the equilibrium vapour pressures of the LiCl, LiBr, CaCl$_2$ and HCO$_2$K solutions are displayed, based on experimental regression models [19, 20, 40] which are more accurate and reliable than the calculation results by Cisternas-Lam model in Figure 6. In the figure, the considered values of concentration for the different desiccant solutions are able to ensure good dehumidification while avoiding any crystallization issue. As previously seen, the solutions able to better dehumidify are LiBr and LiCl solutions. The HCO$_2$K solution shows a better dehumidification ability than the more commonly used CaCl$_2$ solution.
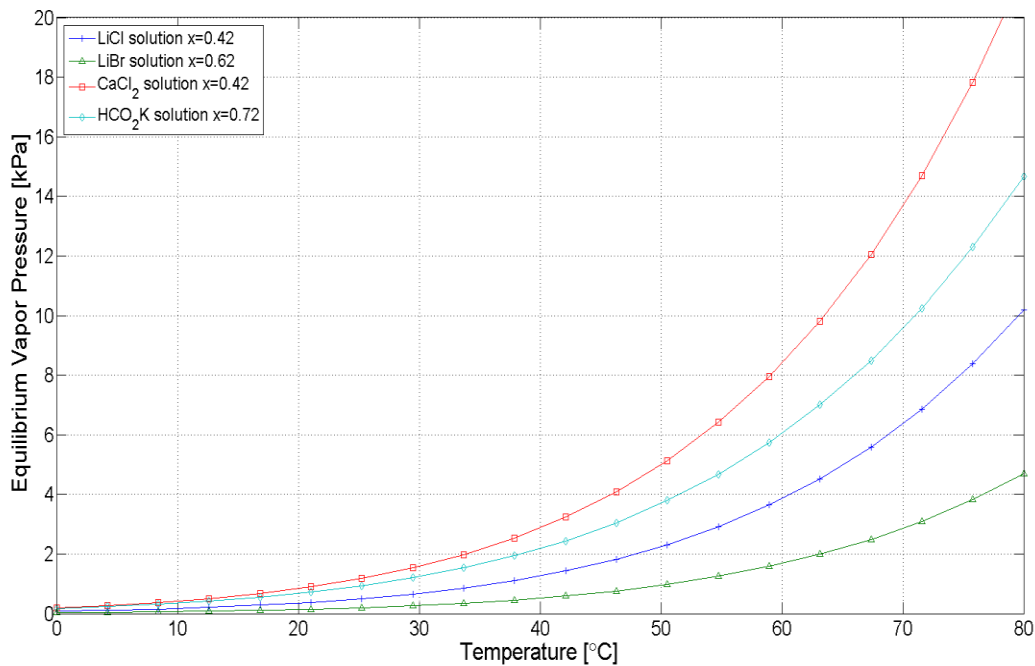
Figure 7 Experimental equilibrium vapour pressure of LiCl, LiBr, CaCl$_2$ and HCO$_2$K solutions.

In Figure 8 and Figure 9, the effect of different concentration and temperature conditions on the equilibrium vapour pressure of LiCl solution is displayed based on Conde's model [19], respectively. The figures show a directly proportionality of the equilibrium vapour pressure with temperature and an inverse proportionality with concentration.
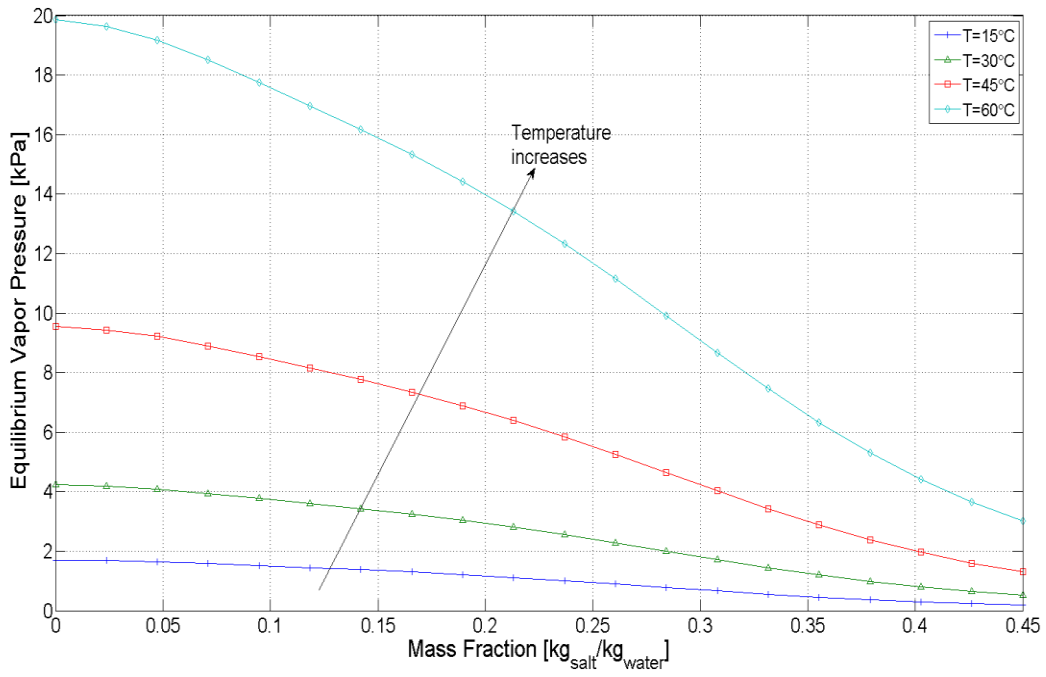
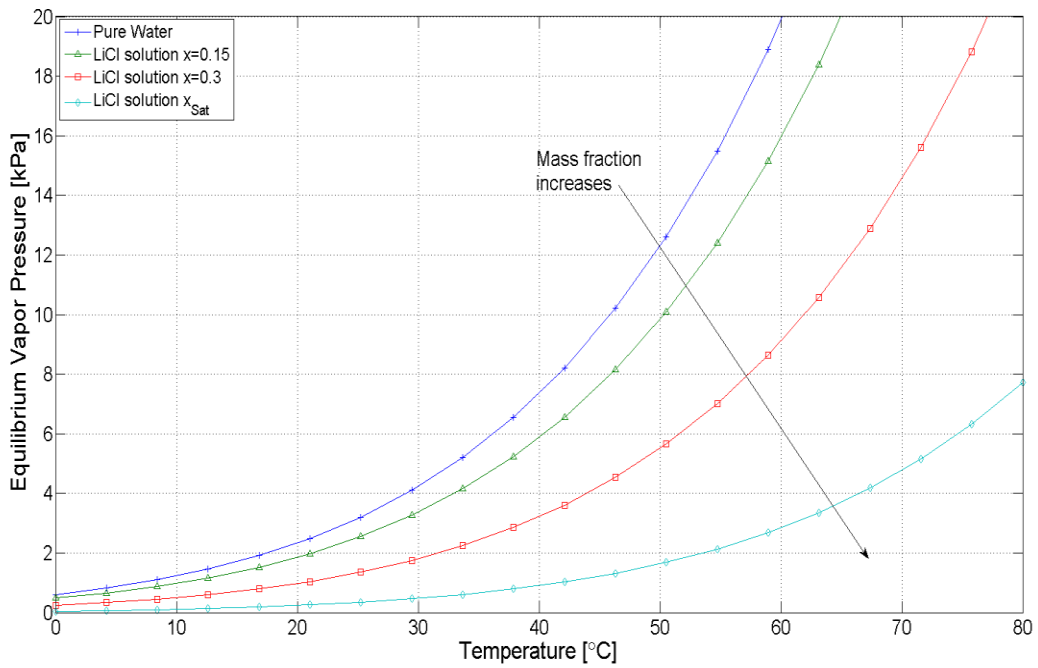Figure 8 Equilibrium vapour pressure of LiCl solution at different mass fractions.

Figure 9 Equilibrium vapour pressure of LiCl solution at different temperatures.

During the dehumidification process, as the desiccant solution increases its moisture content by absorbing the water vapour from the air, latent heat is released and the temperature of the solution increases. This results in a huge decrease in the dehumidification ability of the desiccant solution. For this reason, internally-cooled liquid desiccant dehumidifiers have been developed in order to remove the sensible heat from the liquid desiccant solution while absorbing the latent heat, keeping the fluid temperature constant [55]. An alternative possible solution to overcome this problem is the utilization of a fluid with high specific heat capacity, able to downgrade less its dehumidification ability with a less increase in temperature (see Section 3.3.1).

Conversely, the regeneration/desorption of the desiccant solution is the opposite process to the dehumidification. In the regenerator, the transfer of water molecules to the scavenging air is driven by the difference between the high equilibrium vapour pressure of the solution and that of the air. Therefore, the higher the equilibrium vapour pressure of the solution, the better the desorption process. This property influences the temperature required for the regeneration of the desiccant. The higher equilibrium vapour pressure of the $CaCl_2$ and HCO_2K solutions implies that these solutions require a relatively lower temperature for the regeneration process, as shown in Table 2. Ideally, the perfect desiccant solution would have a lower equilibrium vapour pressure in the dehumidification temperature range (about 15-25 °C) and higher equilibrium vapour pressure in the regeneration temperature range (55-70 °C). Liquid desiccants with a higher equilibrium vapour pressure at the regeneration temperature could potentially be reactivated at lower temperatures (about 45 °C), widening the opportunity for LDAC systems of exploiting low-grade heat.

Table 2 Equilibrium vapour pressure at dehumidification and regeneration conditions for common desiccants.

	Dehumidification (T = 20 °C)		Regeneration (T = 60 °C)	
	Mass Fraction	Equilibrium Vapour	Mass Fraction	Equilibrium Vapour

	[% wt.]	Pressure [kPa]	[% wt.]	Pressure [kPa]
LiCl	0.42	0.3497	0.38	5.2703
LiBr	0.62	0.1327	0.58	2.6412
$CaCl_2$	0.42	0.8341	0.38	10.1853
HCO_2K	0.72	0.6694	0.68	7.043

Because of the dependence of the dehumidification ability on the solution concentration, the concentration of the regenerated solution should be as close as possible to saturation to obtain the best dehumidification performance. However, a working condition too close to the saturation concentration could result in the crystallization, which must be strictly avoided. In fact, when the concentration of the solute in the solution reaches its maximum level, it starts to precipitate. This phenomenon has negative effects on the pumping power, with potential problems of clinging and clogging of the piping network. If this condition persists, the solid precipitate can completely clog the flowing system and stop the flow [56]. Moreover, the crystallization is responsible for a reduction of the surface area for the heat/mass transfer between the air and desiccant [57]. Therefore, the desiccant solution must not crystallize in the temperature and concentration operating range of LDAC system. Figure 10 shows the crystallization line of LiCl solution as the function of solution concentration [18].
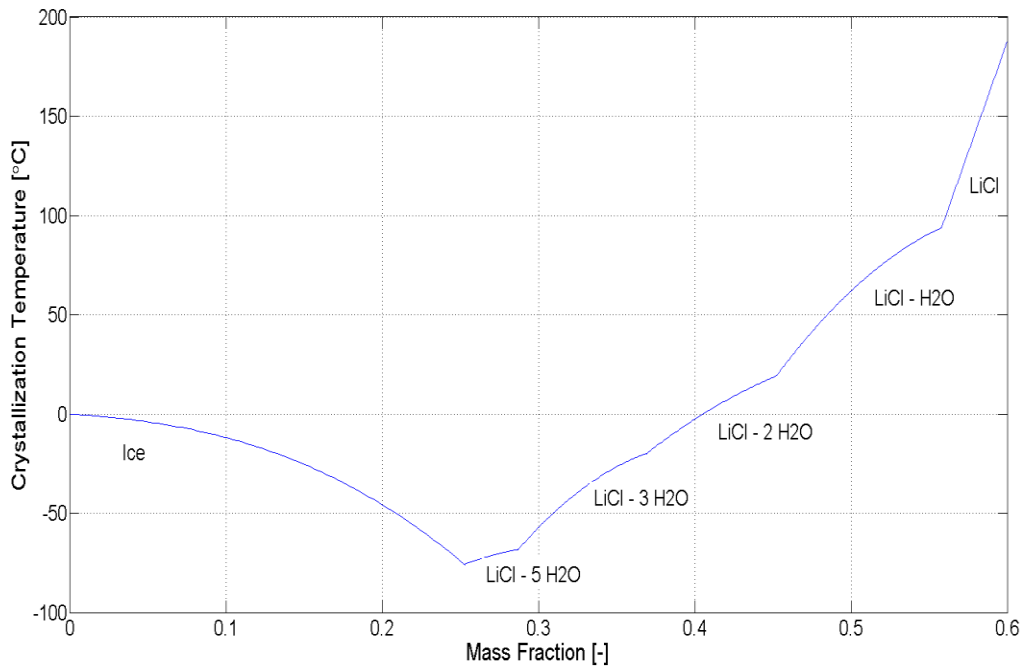
Figure 10 Solubility boundary of LiCl-water mixture [18, modified].

The crystallization limit could be possibly reached in LDAC system for the concentrated solution exiting from the regenerator. The process begins when the solution increases its concentration or its temperature is reduced beyond the limit value for crystallization. As the hot concentrated solution enters the regenerator after the heating source, it desorbs water molecules to a scavenging air stream, decreasing its temperature. If the solution concentration is close to saturation, a decrease in temperature could result in crystallization. Therefore, the regenerator is the most critical component for crystallization control and must be designed to not allow the solution to reach the crystallization limit values of both temperature and concentration. The ambient air condition also plays an important role in the crystallization phenomenon. Liao and Radermacher [58] have discussed how ambient air with high temperature could favour the crystallization process.

Crystallization control can be achieved by employing those desiccant solutions less likely to crystallize, i.e. with a higher saturation concentration, lower crystallization temperature, etc., or by the utilization of

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chemical crystallization inhibitors [59, 60]. Analysing the solubility data for the considered desiccant solutions [61], HCO_2K solution is considered as the solution less likely to crystallize, immediately followed by NH_4NO_3 solution. On the other hand, $MgCl_2$ solution is the one that requires more control to prevent the crystallization. Another possibility to avoid the crystallization is to obtain a higher heat/mass transfer using a better performing contact surface/structure between air and desiccant solution [62]. Current commercial LDAC technologies employ control systems which are able to identify any crystallization issues and take appropriate action against it. However, this technological solution results in an increase in the system cost.

Crystallization is also secondarily affected by the system design and operational factors. In fact, the different possible configuration of the air/solution flow in the system (e.g. cross-flow, counter-flow, parallel-flow) plays a role in the precipitate formation in the solutions. The counter-flow configuration has proven as the best configuration for supressing the crystallization [31]. To conclude with, the cooling tower or chilled water unit of LDAC system must be designed to avoid crystallization. This is particularly important in hot and humid climates, where at the moment expensive wet cooling towers and complex system controls are employed to avoid crystallization. A desiccant solution that is less likely to crystallize could result particularly beneficial in this climate because it allows the use of air-cooled cooling tower [63].

3.1.2 Equilibrium moisture content and relative humidity

Once defined the equilibrium vapour pressure of a desiccant solution, P_{sol}, it is then possible to calculate the equilibrium moisture content, ω_{eq}, defined as:

$$\omega_{eq} = \frac{0.62198\, P_{sol}}{P_{atm} - P_{sol}} \tag{1}$$

The equilibrium moisture content is representable on a psychometric chart and indicates the maximum theoretical amount of water vapour that can be absorbed by a desiccant solution in equilibrium with the

process air. Figure 11 shows ω_{eq} for LiCl, LiBr, and CaCl$_2$ solutions at saturated concentration at 25 °C. The equilibrium vapour pressure of the solutions is calculated based on [19, 20].
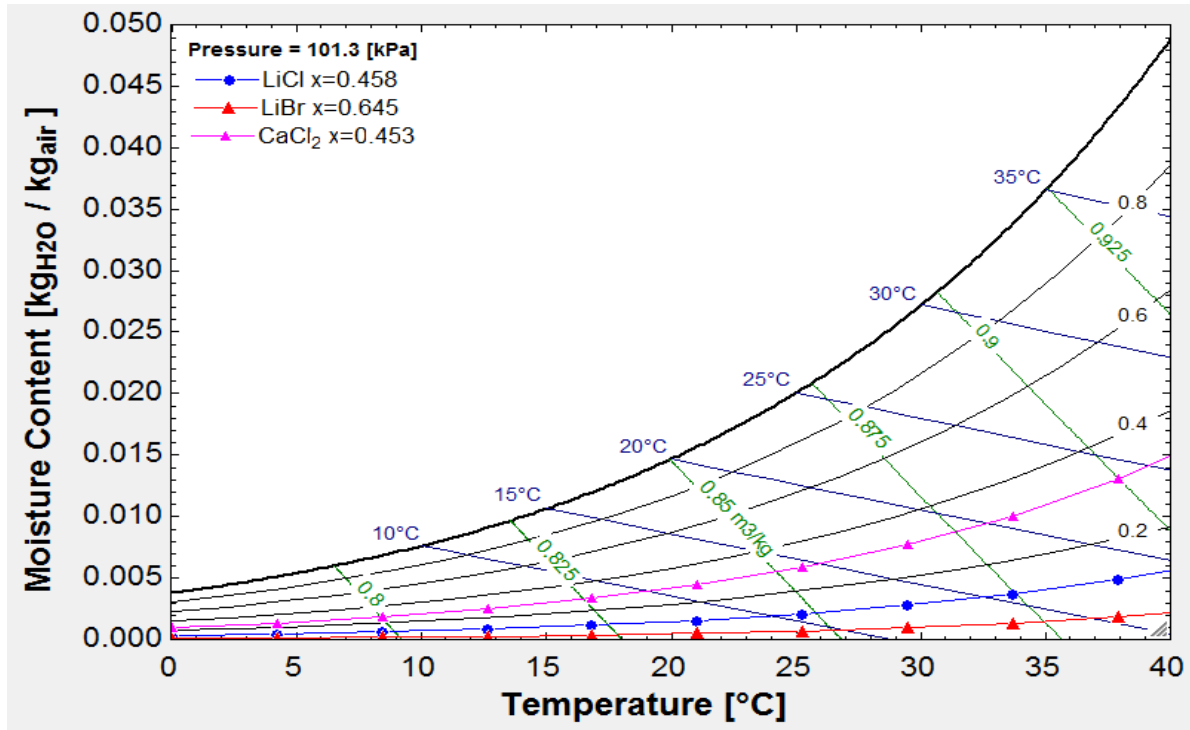

Figure 11 Equilibrium moisture content at saturated concentration at 25 °C of LiCl, LiBr and CaCl$_2$ solutions in psychometric chart.

The psychometric chart in Figure 11 shows how the lowest ω_{eq}, i.e. highest dehumidification ability, is reached by a LiBr solution. However, this dehumidification effect is obtained with a relatively higher solution concentration (64.5% wt.). The dehumidification ability of a LiCl solution is close to that of LiBr but with a lower concentration (45.8% wt.). This is one of the main reasons that makes LiCl solution the most popular desiccant in LDAC systems.

Related to ω_{eq}, the equilibrium relative humidity (ERH) is another parameter indicating the dehumidification ability, representing the theoretical minimum relative humidity the desiccant solution can dry the air. The ERH of some saturated salt solution at 25 °C was evaluated by Greenspan [64], as

presented in Table 3. From the figures shown in the table, the salt solution able to dehumidify the most the air is the caesium fluoride solution which can dehumidify up to very dry conditions (about 3.4% RH). Among the desiccants shown in the Table, LiBr, LiCl, LiI, CH₃CO₂K, and MgCl₂ have been considered as possible liquid desiccant for air-conditioning application as considering other factors such as possible corrosion to metals (ad example of the fluoride group) and toxicity.

Table 3 ERH of some saturated salt solutions at 25 ºC [64].

Salt	RH [%]	Saturation concentration at 25 ºC [65]
Caesium Fluoride (CsF)	3.39 ± 0.94	0.851
Lithium Bromide (LiBr)	6.37 ± 0.52	0.644
Zinc Bromide (ZnBr)	7.75 ± 0.39	0.830
Potassium Hydroxide (KOH)	8.23 ± 0.72	0.547
Sodium Hydroxide (NaOH)	8.24 ± 2.1	0.500
Lithium Chloride (LiCl)	11.3 ± 0.27	0.458
Calcium Bromide (CaBr₂)	16.5 ± 0.2	0.610
Lithium Iodide (LiI)	17.56 ± 0.13	0.623
Potassium Acetate (CH₃CO₂K)	22.51 ± 0.32	0.722
Potassium Fluoride (KF)	30.85 ± 1.3	0.501
Magnesium Chloride (MgCl₂)	32.78 ± 0.16	0.359

3.1.3 Water activity and colligative properties

The water activity a_w is another property that can be used for the evaluation of the de/humidification potential of a desiccant solution. This property is derived from the fundamental principles of thermodynamics and physical chemistry and it represents the amount of water that can be "easily" used in a solution [66, 67]. More solute in the solution results in an increase of the interaction between the water and the solute molecules, meaning that less water is "free" for evaporation in the solution. As for the

equilibrium vapour pressure, the addition of solute in the solution always lowers the a_w of the solution. The water activity can be defined as [68]:

$$a_w = f/f_0 \cong P_{sol}/P_{w,s} \qquad (2)$$

where f and f_0 represent the fugacity coefficient of the substance and of the pure material in a standard state, respectively [69]. The fugacity represents the escaping tendency of a component in solution and can be approximated represented by the vapour pressures values under normal working conditions [70]. Therefore, the water activity can be considered as an alternative definition of the ERH, and hence its dehumidification ability. The following alternative definition of water activity should be given to calculate ERH:

$$a_w = \gamma_w \, y_w \qquad (3)$$

where γ_w and y_w represent the activity coefficient of the water in the electrolyte solution and its mole fraction, respectively. γ_w is a dimensionless parameter depending on the partial molar volume and on the average number and strength of the hydrogen bonds in the solution that contains all the non-idealities of the system [68]. This factor can be calculated using the electrolyte models. By using the γ_w of the water in solution, it is possible to back to the equilibrium vapour pressure P_{sol} of the desiccant solution and then ERH and dehumidification ability.

When an ionic compound, as for example a salt, is diluted in a solution, ions are produced. In the salt solution, the ions strongly interact with each other and with the solvent through electric charges, resulting in a deviated behaviour from an ideal solution characterised by long-range and short-range effects [71]. The water activity is one of the parameters which can be used to quantify the solution's deviation from an ideal behaviour. In fact, the more a desiccant salt is dissolved in water (i.e. lowering a_w), the more the solution's behaviour will not follow the Raoult's law for the partial vapour pressure of each component in an ideal mixture of liquids.

The activity coefficient represents the non-ideality of the solution [72]. If γ_w approaches 1, then the solution behaves as if it were ideal. The addition of molecules of solute to the solution results in vapour pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure (Φ) increase.

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These properties are known as colligative properties and are related to the different thermodynamic behaviour of the real salt solution against the ideal one. The analysis of all these properties can lead to the identification of the dehumidification potential of a solution. The osmotic coefficient influences the hydrophobicity/hydrophilicity of a material [73].

Several electrolyte theories have focused on the determination of water activity, activity coefficient and osmotic pressure of electrolyte solutions, such as Pitzer's model [74, 75], Debye-Huckel model [76, 77] and e-NRTL model [78, 79], etc. All these theoretical models are based on the attempt of determining the non-ideal behaviour of electrolyte solutions caused by the ionic electrostatic forces inside them. These models have been employed to indirectly determine the equilibrium vapour pressure of liquid desiccant solutions, such as in [3, 80-83]. Particularly, the e-NRTL model was considered as a feasible method to determine the thermodynamic properties of electrolyte solutions and of multicomponent mixtures of salts in electrolyte solutions [83]. This is due to the relative easiness in the determination of its parameters, which has led to its use for several applications and its implementation in commercial software, such as ASPEN Plus [84]. The e-NRTL model is based on the evaluation of the short-term and long-term forces present in an electrolyte solution. The long-range contribution calculation is based on the conventional electrostatic theory, represented by the Pitzer-Debye-Huckel model [85]. Accordingly, this model is useful for the calculation of the equilibrium vapour pressure of alternative solutions employable in LDAC systems, such as ionic liquids [86].

3.2 Density, viscosity and electrical consumption

One of the key advantages of LDAC technology respect conventional vapour-compression system is the reduced electricity consumption, since the electric consumption of LDAC systems is only due to the pumping of the solution through the system and the blowing of the air through the dehumidifier/regenerator. Despite being significant, these savings are dependent on the type and thermodynamics of the used desiccant solution.

The fan power consumption is dominated by the air-side pressure drop in the dehumidifier/regenerator. This pressure drop is a fundamental variable in the design of the system, which is dominated by the structure of the air/solution contact surface (random and structured). Gandhidasan [87] calculated the irrigated pressure drop ΔP_f different packed bed configurations, as:

$$\Delta P_f = \frac{\rho_{sol}g}{2988h_b}\sqrt{249h_b(\sqrt{X} - 60\epsilon - 558h_b - 103d_{eq}a_p)} \tag{4}$$

where g is the gravitational acceleration constant (m²/s), ρ_{sol} is the density of the desiccant solution (kg/m³), ϵ is the void fraction of packing (dimensionless), X is the coefficient for the calculation of the pressure drop (dimensionless), d_{eq} is the equivalent diameter (m), a_p is the surface area per unit volume of the packing (m²/m³), and h_b is the operating holdup. For a better understanding of the variables used in the equation, see [87]. ΔP_f is strongly dependent on the factor h_b defined as:

$$h_b = 3.6\left(\frac{U_{sol}a_P^{0.5}}{g^{0.5}}\right)^{0.66}\left(\frac{\mu_{sol}a_P^{1.5}}{\rho_{sol}g^{0.5}}\right)^{0.25}\left(\frac{\sigma_{sol}a_P^2}{\rho_{sol}g}\right)^{0.1} \tag{5}$$

This factor is dependent on the type and structure of the packing (represented by a_p) on the solution velocity (U_{sol}) and on the thermo-physical properties of the desiccant solution, namely the density, dynamic viscosity and surface tension. Apart from the thermodynamic properties, Gandhidasan found out that the lower pressure drop can be obtained with structured packing [87].

The power to pump the desiccant solution through the system is the other electric consumption in LDAC system. The thermodynamic properties affecting this consumption are density, viscosity, and volume of the solution [18]. In Figure 12, the densities of LiCl, CaCl₂, LiBr and HCO₂K solutions are shown [19, 20, 40]. It is desirable for have a solution with the lowest density possible to reduce fan blowing and pumping consumption. The dynamic viscosity is a fluid property defined as the measure of the internal friction of a fluid [18]. The higher the dynamic viscosity, the lower the tendency of the liquid to flow, which will result in a higher pumping power or larger pipes and system volume. Figure 13 shows the dynamic viscosity of the considered desiccant solutions as the function of temperature [19, 20, 40]. It is desirable a solution with the lowest dynamic viscosity to reduce pumping cost. Furthermore, the solution volume also affects the pumping power of LDAC system. The parameter mostly impacting the solution volume is the

concentration difference between concentrated and diluted solution. This quantity is influenced by the moisture absorption rate of the solution (thermodynamic property of the fluid) and by the ratio between air and liquid mass flow rate (system property). On the other hand, low-flow systems characterised by a lower ratio between the solution and the air flow rate (i.e. a higher concentration difference for the solution between inlet and outlet) results in a lower electric consumption respect high-flow systems [88]. Furthermore, any crystallization of the solution must be strictly avoided because it will negatively affect the pumping power and could cause the machine interruption.
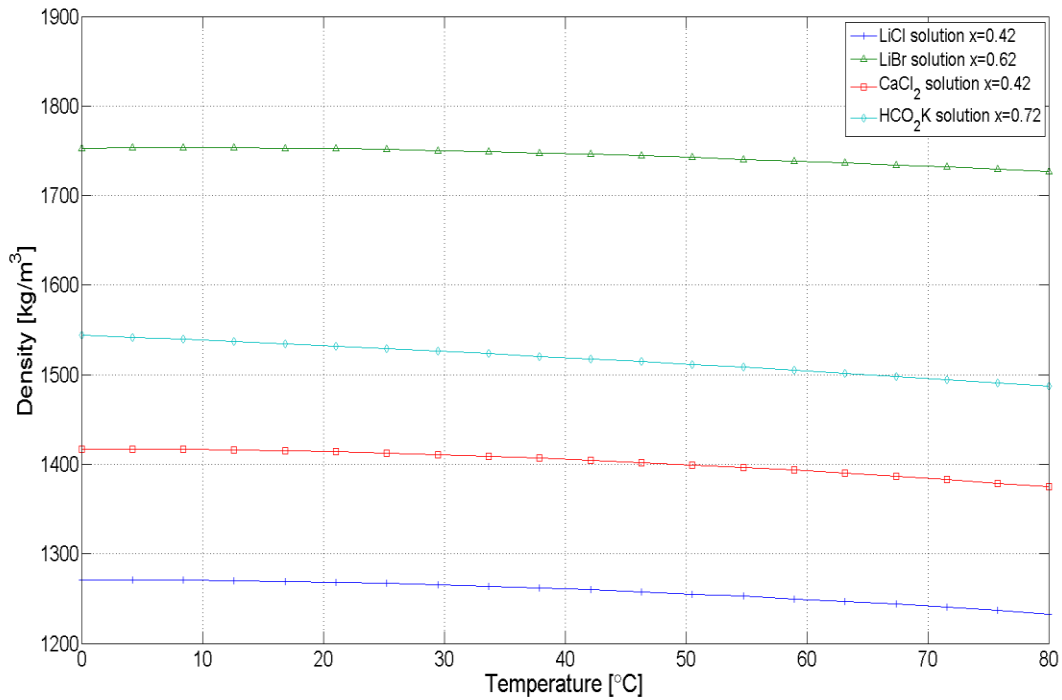
Figure 12 Density of different desiccant solutions at dehumidification operating concentration.
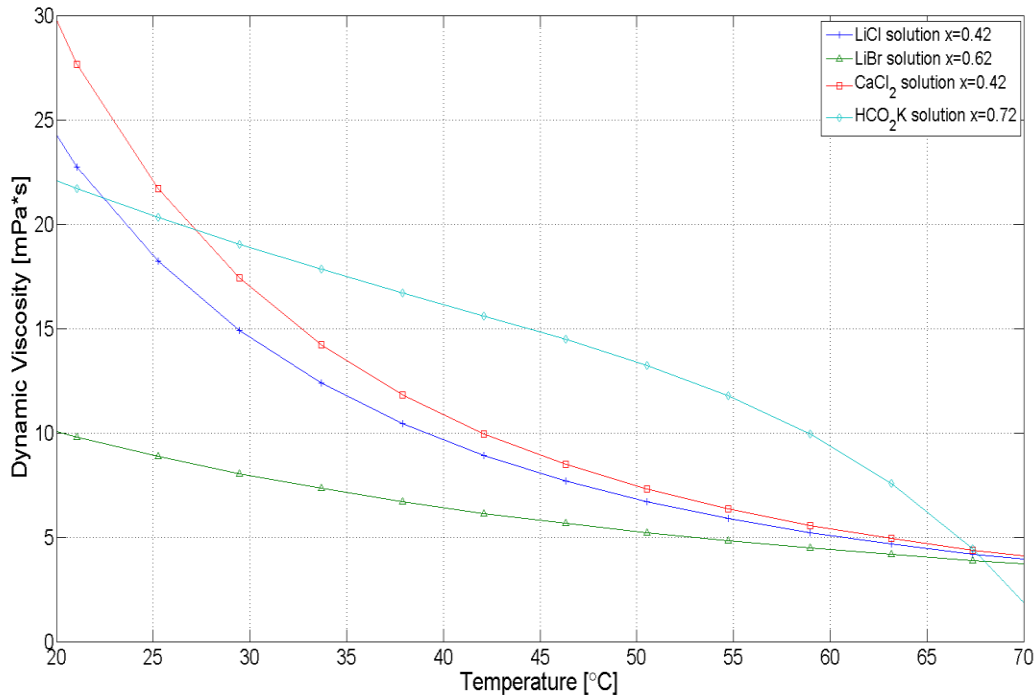
Figure 13 Dynamic viscosity of different desiccant solutions at dehumidification operating concentration.

3.3 Other thermodynamic properties

Other thermodynamic properties of the liquid desiccant play a secondary role in the determination of the overall performance of LDAC system and are here briefly described. The determination of a complete set of thermodynamic properties of the solutions is useful in the development of a heat and mass transfer mathematical model and enhancement of the performance in LDAC system.

3.3.1 Specific heat capacity

The specific heat capacity of the solution is a property representing the change of temperature in the solution, related to energy transfer. The absorption process in the dehumidifier is an exothermic process that releases heat, the transfer of water molecules from the air to the desiccant solution increases the temperature of the solution; however, as shown in Section 3.1.1 the dehumidification ability of the desiccant solution drops significantly as the temperature increases. A solution with a higher value of

specific heat capacity is favourable because this implies that the temperature increases less, making the dehumidification process more stable. The Figure 14 shows the specific heat capacity of desiccant solutions at dehumidification operating concentrations [18, 19, 39]. Once again, LiCl solution shows the best characteristics as desiccant solution for the dehumidification process.
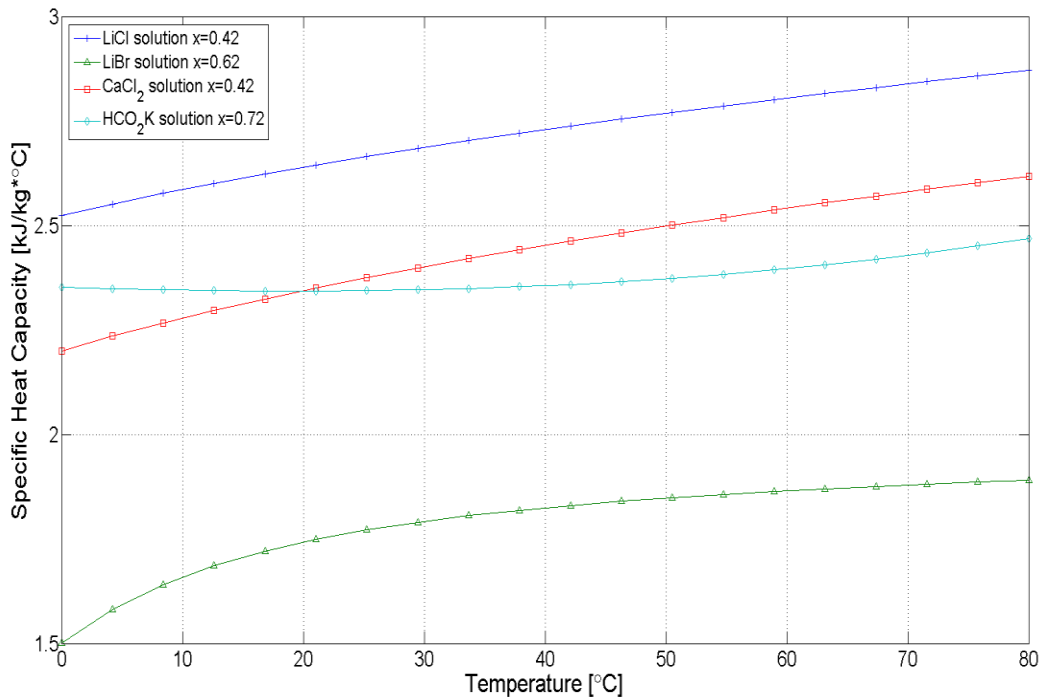

Figure 14 Specific heat capacity of different desiccant solutions at dehumidification operating conditions.

3.3.2 Heat of absorption

The absorption process in the dehumidifier is an exothermic process that releases heat, known as the absorption heat Δh_{abs} [21]. The value of Δh_{abs} is higher than the condensation heat of pure water vapour. The difference between these two values is called enthalpy of mixing (or enthalpy of dilution) [19], which can be defined as the heat produced by the absorption of water vapour molecules by the desiccant solution at constant composition. The higher the heat of mixing, the higher Δh_{abs}. The heat of absorption is

dependent on the concentration and inversely proportional to the temperature, as can be seen in Figure 15 using LiCl solution [19].
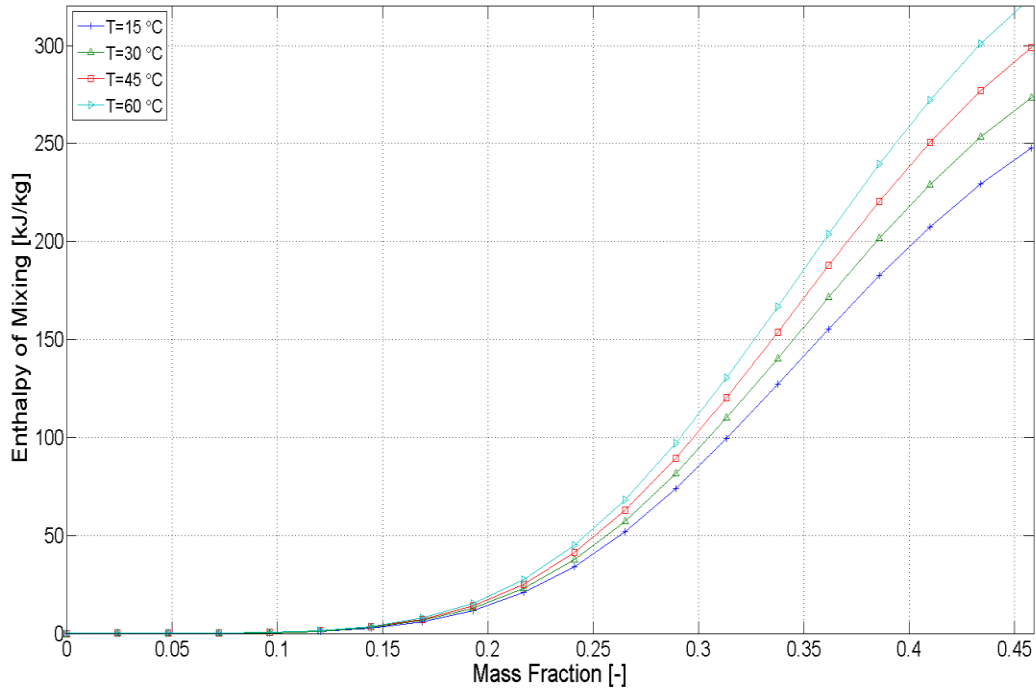

Figure 15 Enthalpy of mixing of LiCl solution depending on concentration and temperature [19, modified]

A solution with higher Δh_{abs} becomes warmer during the dehumidification process, degrading the moisture removal ability of the desiccant solution. Internally-cooled dehumidifiers are therefore necessary to improve the dehumidification performance of desiccant solutions with high Δh_{abs}. A solution with higher Δh_{abs} requires more powerful cooling tower/chilled water unit of LDAC system that must be lowered to cyclically process the solution [89]. However, the heat of mixing of common desiccant solutions is significantly lower than the heat of water condensation, so that Δh_{abs} of the dehumidification process of different common desiccant solutions are very close and the corresponding temperature increments are dominated by the liquid specific heat capacity [90]. However, the mixing heat can be a

non-negligible part of Δh_{abs} in some ionic liquids, which causes further temperature increment in the dehumidification process.

The Clausius-Clapeyron equation can be used to approximately describe the relationship between the heat of absorption and the temperature-dependent equilibrium vapour pressure of the desiccant solution [91]:

$$\frac{\Delta h_{abs}}{R_w} = \frac{\lambda + L}{R_w} = \frac{d[\ln(P_{sol})]}{d[-1/T]} \tag{6}$$

where R_w is the specific gas constant of water vapour, λ is the enthalpy of vaporization of water, L is the enthalpy of mixing, and T is the temperature with the unit of K. The above equation can be illustrated by the curve $\ln(P_{sol})$ vs $-1/T$, as shown in Figure 16, which shows LDAC thermodynamic cycle on a Van't Hoff diagram with a LiCl solution, considering a 4% variation between concentrated (42% wt.) and diluted (38% wt.) solution for an internally cooled/heated LDAC system (i.e., no increase/decrease of the temperature of the solution during de/humidification process). The temperature of the dehumidification and regeneration process are considered 15 °C and 60 °C, respectively. To evaluate the different absorption/desorption potential of the solutions, the figure also shows the partial pressure of water vapour in ambient air at 20 °C and 65% RH. A different value of Δh_{abs} results in a different slope in the qualitative Van't Hoff diagram [91].
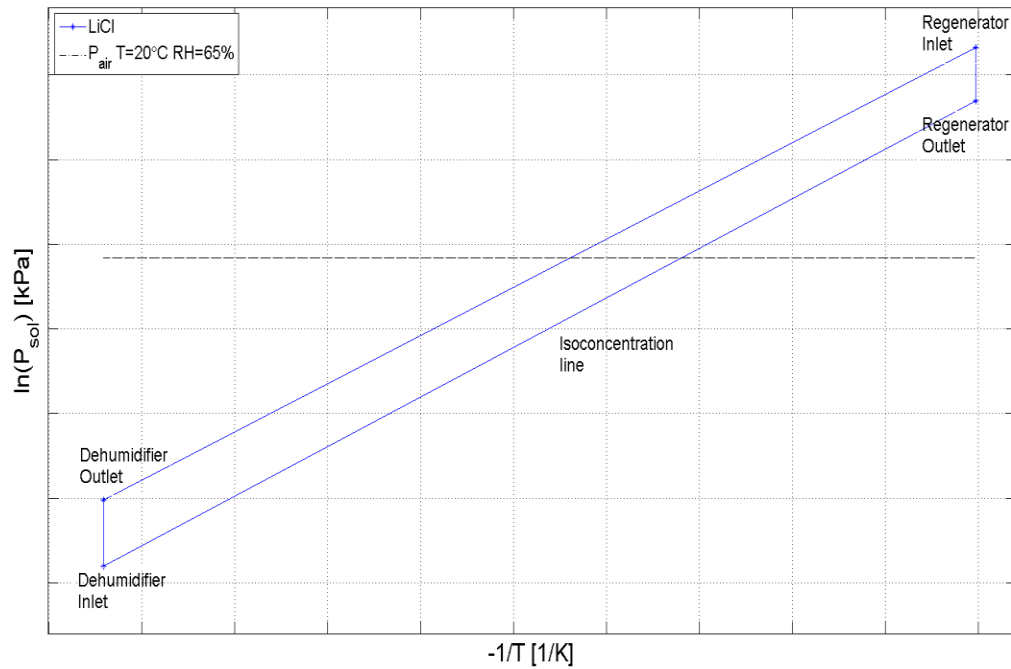
Figure 16 Qualitative Van't Hoff diagram for LDAC process cycle.

Under the given conditions, the Van't Hoff diagram in Figure 14 shows how the LiCl solution is able to efficiently perform both the dehumidification and regeneration process because of the sufficient pressure difference between the desiccant solution and the partial pressure of the water vapour in the ambient air. A higher slope of the iso-concentration line could enhance the absorption and desorption process by increasing the pressure difference between desiccant solution and air, but this could result in possible crystallization for the concentrated solution exiting from the regenerator [91]. As mentioned, the qualitative Van't Hoff diagram was obtained considering a gradient concentration of 4% between concentrated and diluted LiCl solution, nevertheless, the use of different desiccant solutions and system configurations result in a different concentration gradient between concentrated and dilute solution, resulting in a different slope of the Van't Hoff diagram for LDAC cycle.

3.3.3 Heat and mass transfer coefficients

The dehumidification and regeneration process is a heat and mass transfer process involving sensible heat transfer due to heat conduction and latent heat transfer due to water vapour diffusion [37]. The heat and mass transfer coefficient determination is fundamental for the optimization of the absorption/desorption and cooling/heating process of LDAC system. Three types of numerical models are commonly employed for the analysis of the heat and mass transfer in LDAC system: the finite difference method [92, 93], the effectiveness-NTU model [94], and a model based on fitted algebraic equations [95]. These numerical methods require the calculation of the heat and mass transfer coefficients. Several studies have focused on the determination of heat and mass coefficients for LDAC systems [96-101], which is based on operational parameters, i.e. air/desiccant contact surface and flow configuration (counter, cross or parallel flow), and thermodynamic and transport parameters of both ambient air and desiccant solution.

One of the effectiveness models mostly developed is the NTU-Le model [100]. In this model, the overall heat and mass transfer is calculated depending on the dimensionless parameters, Lewis number (Le) and NTU (Number of Transfer Unit), defined as:

$$Le = \frac{h_h}{h_m c_{p,a}} \tag{7}$$

$$NTU = \frac{h_m a_P V}{m_a} \tag{8}$$

where V is the volume of the packing material [m^3], h_h is heat transfer coefficient [W/(m^2 °C)], h_m is mass transfer coefficient [kg/(m^2 s)]. The Le number is usually assumed equal to 1 for LDAC process [101], while the evaluation of NTU has been performed with different strategies [94]. The determination of the heat and mass transfer coefficients is based on experimental experiences. Gandhidasan et al. [97] determined the heat and mass transfer coefficients in a packed tower dehumidifier, using CaCl$_2$ solution as desiccant and Raschig rings and Berl saddle as packing material. Chung et al. [98] developed a complete analysis of the heat and mass transfer coefficients in random and structured packing with LiCl solution based on the Buckingham-Pi method, their correlation showed the higher heat transfer coefficient for a randomly packed column.

Several studies have focused on the correlation of the *Nu* and *Sh* number with experimental data to calculate the heat and mass transfer coefficient of the process [99, 101]. The heat and mass transfer coefficient can be correlated to *Nu* and *Sh* through the relation [100]:

$$Nu = \frac{h_h d_{eq}}{k} \tag{9}$$

$$Sh = \frac{h_m d_{eq}}{\rho_a D_a} \tag{10}$$

The heat and mass transfer coefficient correlations for the dehumidification process in LDAC systems are summarised in Table 4 and Table 5, respectively.

Table 4 Correlations for heat transfer coefficient in the dehumidification process.

Author	Correlation	Desiccant	Packing type
Gandhidasan [97]	$h_{hg} = \left[1.195\, F_a\, c_{p,a}(d_{eq} m_a/v_a(1-\epsilon))^{-0.36}\right]/Pr_a^{0.667}$ $h_{ml} = 25.1\,(k_{sol}/d_{eq})\,(d_{eq} m_{sol}/v_{sol})^{0.45}\, Sc_{sol}^{0.5}$	CaCl₂	Several types
Chung et al. [98]	$h'_m a_p (d_p^2/k_a) = 5.2*10^{-5}\,(1-x)^{1.56}(F_{sol}/F_a)^{0.5}(Pr_a)^{0.333}\,(Re_a)^{1.6}$ $h'_m a_p (d_{eq}^2/k_v) = 2.78*10^{-6}\,(1-x)^{1.8}(F_{sol}/F_a)^{0.4}(Pr_a)^{0.333}\,(Re_a)^{1.6}$	LiCl	Random Structured
Chen et al. [101]	Nu $= 4.7756$ $*10^{-5}(1$ $-\omega_{sol,eq}/\omega_{a,in})^{0.8198}(T_{sol}/T_a)^{0.3846}(m_{sol}/m_a)^{-1.001}(Sc_a)^{0.333}\,(Re_a)^{1.7936}$	LiCl	Structured

Table 5 Correlations for mass transfer coefficient in the dehumidification process.

Author	Correlation	Desiccant	Packing type
Onda et al. [96]	$h_m = 5.23\,(a_p D_a/R\,T_a)(F_a/a_P\, v_a)^{0.7}(v_a/D_a\,\rho_a)^{1/3}(a_P d_P)^{-2}$	Organic, inorganic	Random

Gandhidasan [97]	$h_{mg} = \left[1.195\, F_a(d_{eq}m_a/v_a(1-\epsilon))^{-0.36}\right]/Sc_a^{0.667}$ $h_{ml} = 25.1\,(D_{sol}/d_{eq})\,(d_{eq}m_{sol}/v_{sol})^{0.45}\,Sc_{sol}^{0.5}$	CaCl$_2$	Several types
Chung et al. [98]	$Sh = 1.326 * 10^{-4}\,(1-x)^{-0.94}(F_{sol}/F_a)^{0.27}(Sc_a)^{0.333}\,(Re_a)^{1.16}$ $Sh = 2.25 * 10^{-4}\,(1-x)^{-0.75}(F_{sol}/F_a)^{0.1}(Sc_a)^{0.333}\,(Re_a)$	LiCl	Random Structured
Chen et al. [101]	Sh $= 7.3492$ $* 10^{-7}(1$ $-\omega_{sol,equ}/\omega_a)^{-0.8956}(T_{sol}/T_a)^{0.2376}(m_{sol}/m_a)^{0.5235}(Sc_a)^{0.333}\,(Re_a)^{2.1576}$	LiCl	Structured

As shown in Table 4 and 5, the thermodynamic properties of the desiccant solution involved in the process include equilibrium vapour pressure, density, viscosity, specific heat capacity, thermal conductivity, diffusion coefficient of water vapour into the solution, and Henry's law constant [19, 97, 98, 102]. The correlations show how the mass flow rate (air and solution), ambient air, and air/solution surface contact affects the heat and mass transfer. In Chung's correlation [98], the influences of the desiccant solution concentration on the heat and mass transfer process is expressed. The improvement of mass transfer resulting by a higher desiccant solution concentration is obvious, which leads to a lower equilibrium vapour pressure and hence a higher absorption ability. On the other hand, a higher concentration solution results in a decrease of the heat transfer. This is due to the increase of dynamic viscosity of the desiccant solution that reduces the heat transfer from the gas phase to the liquid one [98].

A good desiccant solution should be able to ensure a high heat and mass transfer to facilitate the dehumidification and regeneration process. One of the adopted solutions to enhance the air/desiccant heat and mass transfer is the addition of nanoparticles. Ali et al [103] demonstrated the improvement of heat and mass transfer by the addition of Cu-ultrafine particles, represented by the Nusselt and Sherwood number. Moreover, the type and material of the contact surfaces of the dehumidifier and regenerator strongly affects the heat and mass transfer process. LDAC contactors can be classified as direct-contact and indirect-contact. The most common direct-contact dehumidifier/regenerator are: packed bed, spray

tower, falling fluid, etc. [104, 105], while the indirect-contact technology has been recently developed [1] and will be briefly described in Section 3.5.1. Furthermore, a low surface tension desiccant solution can improve the heat and mass transfer because of the higher wetting of the contact surface [106]. The desiccant solutions present a higher surface tension comparing to water, making the wetting of the contactors more complicated. However, for the same high surface tension characteristic, once the contact surface is fully wetted with the liquid desiccant, it will not evaporate out [41]. Oberg et al. [107] reported the surface tension of LiCl, CaCl$_2$, and LiBr solutions. Under the given temperature and composition conditions, the LiCl solution shows the highest surface tension. However, as a matter of fact, the ideal process of dehumidification shown in Section 3.1.2 is never reached because of the insufficient air/solution surface contact and time for the reaction to happen.

3.4 Thermo-chemical energy storage capacity

One of the main advantages of liquid desiccants is their potential as thermo-chemical energy storage medium. The classic energy storage methods, characterised by sensible or latent heat storage, require insulated tanks to eliminate the thermal losses. On the contrary, the thermo-chemical storage with liquid desiccant is almost free-losses due to the fact that the dehumidification and regeneration potential of the solution is delivered only when the solution contacts the air and it absorbs or desorbs water vapour [49]. This property makes feasible the use of storage tanks without any insulation. The free-losses storage also allows the dehumidification and the regeneration side to be on different sites, while the possible transport of liquid desiccant from the available heat source side to the consumer side makes LDAC a novel and promising technological solution for HVAC application. This is recently under study for the employment in district heating networks [49]. On the other side, the storage characteristic makes the liquid desiccant employable when an intermittent heat source is available (e.g. solar energy, etc.) or when the heat source does not match the heating demand, sensibly widening the application field of LDAC technology [108-109].

The thermo-chemical energy storage by liquid desiccant can be achieved by integration of storage tank(s) in LDAC system. When the intermittent heat source is available, the stored dilute solution is pumped from one storage tank to the regenerator and then the obtained concentrated solution is stored in the other tank; when the cooling/dehumidification demand is needed to meet, the concentrated solution is pumped to the absorber, driving the cycle without any further heat needed; once the process is completed, the obtained dilute solution is stored in the dilute solution tank. Sometimes, in reality, one tank was used instead of using two tanks, where the strong and weak solutions were mixed or separated by buoyancy [110]. The energy storage capacity of a liquid desiccant, SC, is defined as [111]:

$$SC = \rho_{sol,dil}\, x_{sol,dil} \left(\frac{1-x_{sol,dil}}{x_{sol,dil}} - \frac{1-x_{sol,conc}}{x_{sol,conc}} \right) \lambda \qquad (11)$$

where $\rho_{sol,dil}$ is the density of solution at the diluted concentration, λ is the latent heat of vaporization, and $x_{sol,dil}$ and $x_{sol,conc}$ are the mass fraction of the diluted and concentrated solutions, respectively. Therefore, the energy storage capacity depends on the concentration and density of the concentrated diluted solution and on the working conditions of LDAC system, namely the concentration difference between the diluted and concentrated solution in the cycle. The latter one is the most important factor in the evaluation of desiccant thermo-chemical storage and it is mostly dependent on the mass flow ratio between air and solution (system property) and on the moisture absorption capacity (fluid property). The comparison between energy storage capacity of liquid desiccant thermo-chemical storage and other common thermal energy storage technologies is shown in Figure 17. Comparing to the classic sensible and latent heat technologies, the thermo-chemical energy storage with liquid desiccant has higher energy density [111-113].
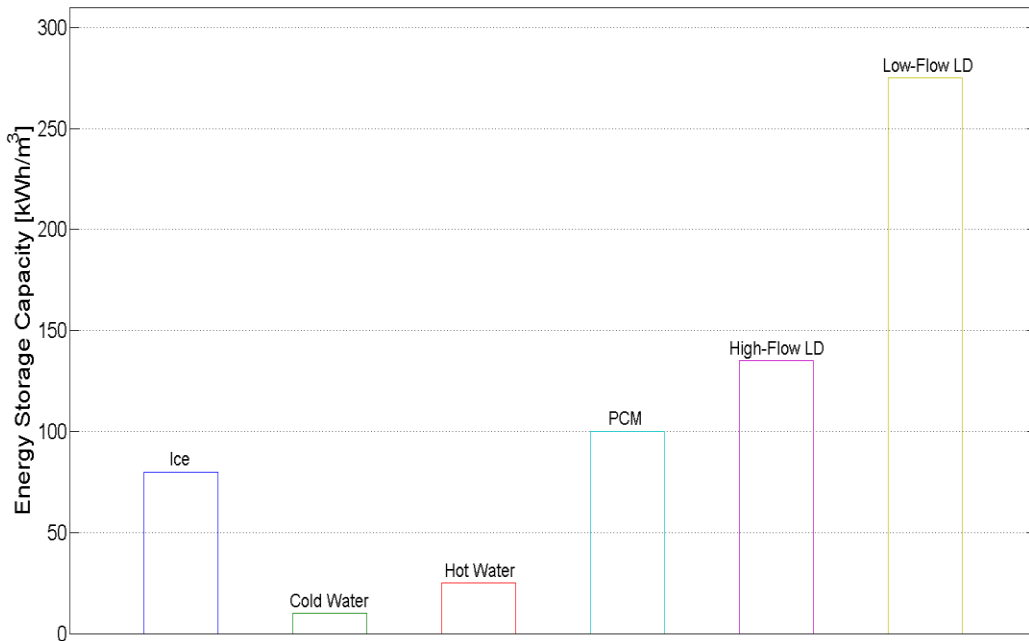
Figure 17 Energy density of the main thermal energy storage technology [111, modified]

As shown in Figure 17, low-flow LDAC systems, characterised by a higher difference in the solution concentration between absorber and regenerator are better performing with thermo-chemical energy storage comparing to the high-flow systems. This is due to the fact that the regeneration process is favoured by a solution with a lower concentration, i.e. higher equilibrium vapour pressure, which eases the regeneration process.

In Figure 18 the *SC* of some desiccants is shown considering a low-flow LDAC system with up to 12% mass fraction difference between the concentrated and diluted solution. Apparently, zero mass fraction difference between the diluted and concentrated solutions indicates non thermal energy storage capacity; and the increase of mass fraction difference leads to larger storage capacity as shown in the figure and hence, again, low-flow LDAC systems are the most favourable for thermo-chemical storage. The $MgCl_2$ solution present the highest storage capacity, followed by $CaCl_2$, LiCl, LiBr, and HCO_2K solutions. The above comparison is conducted based on the same concentration gradient, however, solution characterised

by higher absorption/desorption capacity is more likely to have a higher concentration difference and therefore higher energy storage capacity. The thermo-chemical energy storage capacity is, therefore, also influenced by the thermodynamic properties of the fluid employed. Furthermore, it must notice that a solution too close to the saturation concentration could result in a crystallization problem when there is an ambient temperature variation, therefore LDAC systems integrated with storage tanks must work not too close to the saturation concentration [10, 114].
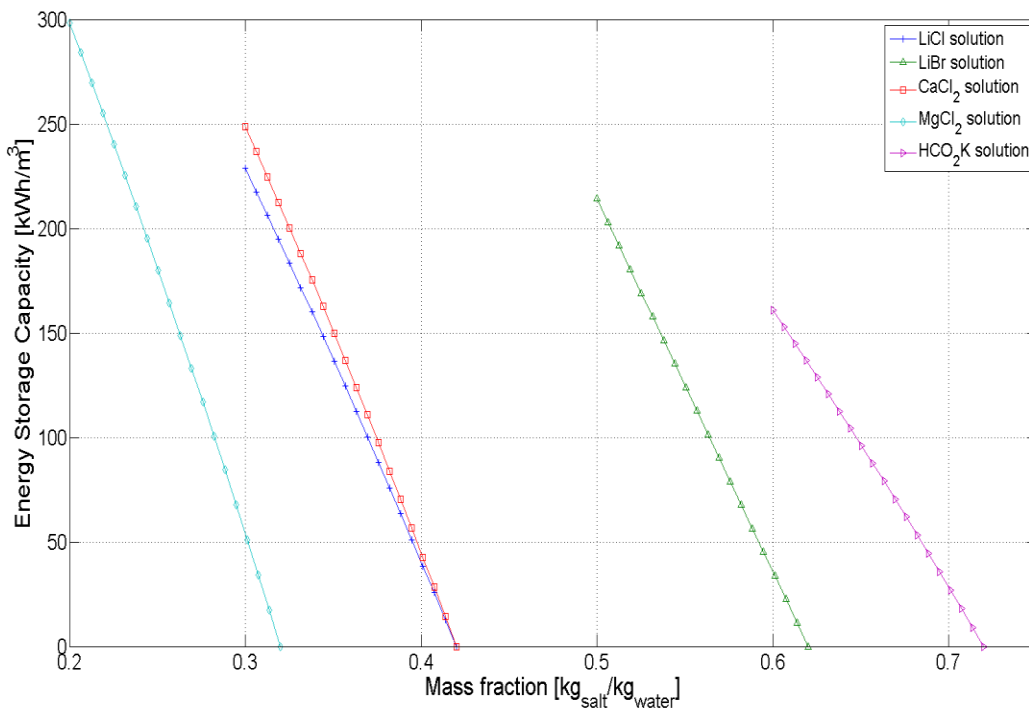

Figure 18 Energy storage capacity of different desiccant solutions in low-flow system.

4. Non- thermodynamic factors

4.1 Health, safety and air quality

The respect of the health and safety requirements is a significant aspect that liquid desiccants used for HVAC application must satisfy. Solutions which possible ingestion, inhalation or skin contact could result dangerous must be avoided. One of the possible parameter for the evaluation of the toxicity is the

lethal dose LD50, namely the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals [89]. The LD50 is one way to measure the short-term poisoning potential (acute toxicity) of a material. The oral LD50 for a mouse after ingestion of common desiccants is presented in Table 6. The figures are taken from the Material Safety Data Sheet of the desiccants [115-119]. The table shows how all the desiccant solutions present a value of LD50 that requires attention, even if not particularly high. In fact, substances with LD50/oral/mouse between 500 mg/kg and 5000 mg/kg are considered slightly toxic, while between 5000 mg/kg and 15000 mg/kg are considered practically non-toxic [120]. Apart from the ingestion, inhalation and skin contact must be checked and avoided.

Table 6 LD50/oral/mouse for common salts used as desiccants.

Desiccant	LD50/oral/mouse [mg/kg]
LiCl	1165
LiBr	1840
$CaCl_2$	1940
HCO_2K	5500
$MgCl_2$	7600

In fact, the ability of desiccant solutions to improve the indoor air quality is considered as one of the main advantages of LDAC technology. This is mainly obtained through three different improvements: reduction of VOCs (Volatile Organic Compounds), removal of bacteria and viruses, capture of PM (Particulate Matter) [121]. First, the desiccant solution provides a bacteriostatic and bactericidal function due the fact that used salts are natural biocide and can remove possible virus or bacteria present in the air [10, 122]. Moreover, the particulate and VOCs capture ability of liquid desiccants cleans the air with beneficial results for the human health. Furthermore, the desiccant dehumidification process does not involve condensation of water vapour below the dew point of the air, which results in the absence of

microorganisms that are breeding in humid conditions, e.g. Escherichia coli, legionella and related illness as Pontiac's fever and Monday's fever [123]. The use of liquid desiccant for HVAC can result in a significant improvement of the indoor air quality in the building. Finally, according to the health and safety requirements, the desiccant used must be non-flammable or reactive. The Material Safety Data Sheet of the considered desiccants showed a good behaviour from this point of view.

As aforementioned, in a direct-contact dehumidifier/regenerator the liquid desiccant solution directly exchanges mass and heat with the air that needs conditioning. Therefore, the carry-over of desiccant solution in the processed air is a possible issue that must be avoided [42]. Common LDAC systems employ mist eliminators to avoid this phenomenon. However, the use of mist eliminators is highly energy-inefficient, which not only increases the overall and maintenance cost of the system but also leads to an increase in the air-side pressure drop, resulting in a higher electricity consumption for blowing the air through the system [41]. In the recent study, new configurations have been developed aiming to overcome the carry-over problem, such as low-flow systems [124] and membrane contactors [125]. The latter solution exploits a membrane permeable to the water vapour but not to the desiccant solution, realizing an indirect contact between the liquid and air, which completely eliminates the carry-over problem. However, the employment of the membrane suffers from the large resistance to the transfer of water vapour between solution and air, and does not exploit the hygiene control property of the salt solutions [1].

4.2 Corrosion

One of the drawbacks of LDAC system is that the commonly employed halide salts in desiccant solutions (LiCl, CaCl$_2$, etc.) are corrosive to metals. This limits the reliability of the system, putting serious issues in term of system longevity and related costs [17], which prevents the worldwide development and utilisation of LDAC systems. In the case of solution carry-over, the corrosion of liquid desiccant will not just influence the piping and the solution heat exchanger, but also any downstream metallic component

involved in the transport of the air, such as ducting, solution heat exchanger, etc., sensibly reducing the lifespan of the equipment [38].

Comparing to closed system, such as absorption chillers, the problem of the corrosion results more important in open systems because of the presence of oxygen and CO_2 in the air that enhances the corrosion rate of most metals [18, 88, 126]. Corrosion is an electrochemical process of destruction of material caused by chemical reactions. The process is based on the loss of electrons from metal, resulting in a deterioration of the material and of its properties [127]. Depending on the metal employed in the system, the pH of the solution is a factor that influences the corrosion of the metal. An acid environment results particularly corrosive for zinc and carbon steel. On the other hand, the corrosion of aluminium is not influenced by the pH of the solution. The intensity of the corrosion process is also dependent on the temperature [123]. The halogen elements (Chlorine and Bromide) presents in the halide salts of desiccant solutions are particularly responsible for an acid pH of the solution and the resulting corrosion phenomenon. Therefore, for high-temperature applications, e.g. LDAC driven by heat recovery from a CHP, the corrosion is a primary issue with desiccants composed by halogen elements and requires particular precautions. For this reason, HCO_2K and $Ca(NO_3)_2$ solutions could perform better in this situation because they are able to ensure good dehumidification performance with limited corrosion.

In recent periods, machines designed to avoid the contact between solution and metal or using a corrosion resistant material, such as titanium or plastic, have been developed. While titanium is expensive, the use of plastic could benefit the economics of the system. The choice of a fluid not or less responsible for corrosion could resolve the corrosion of LDAC systems. One of the used solutions is to add corrosion-inhibitor additives to the liquid desiccant [128]. For example, a pH-buffering agent is added to the LiCl solution to limit the corrosion rate to metals. Alternatively, a solution could be the employment of fluid less-corrosive or not-corrosive at all, such as ionic liquids [129]. These fluids will be described more in depth in Section 6. Moreover, De Lucas et al. [130-132] reported that the addition of HCO_2K to LiBr solution for use in absorption refrigeration system can decrease the corrosion rate to metals due to the alkaline pH of the HCO_2K. Apart from that, the mixing of HCO_2K to LiBr solution improves the

performance of the fluid, lowering its regeneration temperature, density, viscosity, toxicity, etc. It has been shown that the best performance is obtained with a LiBr/HCO$_2$K mass ratio of 2:1.

4.3 Economics of liquid desiccant

The cost of the liquid desiccants and their related availability is another factor that must be accounted for the overall evaluation of the system [81, 83]. The price of the salts used as desiccants in the paper is shown in Table 7 [32]. The prices are taken from [133-137].

Table 7. Price per metric ton of desiccant salt [32, modified].

Salt	Price per metric ton of salt (GBP)	Price per metric ton of anhydrous salt (GBP)	Salt relative cost (based on cost of CaCl$_2$)	Reference dehumidification mass fraction [% wt.]	Solution relative cost
LiCl-anhydrous	6482.02	6482.02	28.9	0.42	12.138
CaCl$_2$-dihydrate	127.68	224.265	1	0.42	0.42
LiBr-anhydrous	2553.5	2553.5	11.386	0.62	7.06
MgCl$_2$-hexahydrous	121.78	555.317	2.476	0.32	0.792
HCO$_2$K-anhydrous	288.35	288.35	1.286	0.72	0.926

As previously shown in Figure 3 and 4, LiCl and LiBr solutions present the lower equilibrium vapour pressure and have better dehumidification ability. Unfortunately, Table 7 shows that these solutions are also the most expensive because of their difficult availability. Moreover, since the development of the Li-ion batteries the price of Lithium-based salts is largely increased [32]. Conversely, CaCl$_2$ and MgCl$_2$ solutions present a lower dehumidification potential but they are extremely cheap and readily available

because produced from industrial processes and as a by-product from seawater processing, respectively [17]. The HCO_2K price still represents a sensible economic saving respect LiCl and LiBr solutions. To be complete, this analysis should also consider that some of these desiccant salts are sold in their hydrate form, as shown in the Table. In addition to that, the relative cost of different desiccant solutions is evaluated considering their mass fraction.

In the past, the possible mixture of salts in desiccant solution to achieve the best compromise between dehumidification ability and cost was investigated [138-140]. Ertas et al. [138] showed that a 50wt. %-50wt. % LiCl-$CaCl_2$ solution performs better from a cost-effectiveness viewpoint. Lychnos et al. [18] investigated the thermodynamic properties of seawater bitterns for employment in LDAC system. Hassan et al. [141] investigated the addition of $Ca(NO_3)_2$ to a $CaCl_2$ solution to stabilize the solution performance. The models to determine the thermodynamic properties of mixture are based on the parameters a_w, Φ and γ_w, calculated by means of the electrolyte theories [3, 80-83].

Analytical determination has been conducted to ensure the best compromise between performance and cost [81, 83]. The desiccant with the lower cost ($CaCl_2$) was assumed as unit cost and the other values were consequently calculated [83]. To evaluate which solution is able to perform better dehumidification considering also an economic viewpoint, an alternative version of the parameter R has been defined and used [83]:

$$R = \frac{Dehumidification\ Effect}{Cost} = \frac{P_{w,s} - P_{sol}}{UnitCost_{salt} * x_{salt}} \tag{12}$$

The parameter R indicates the compromise between dehumidification process and the cost of the solution in the system. The higher R, the better the cost-effectiveness of the solution.
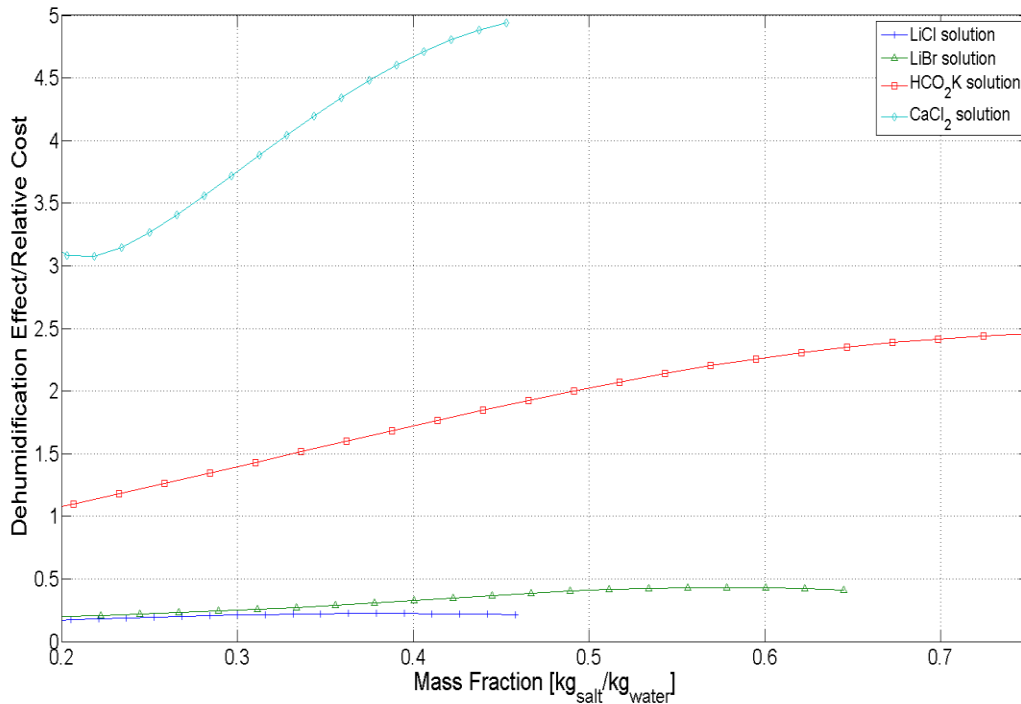
Figure 19 Cost-effectiveness of desiccants solutions.

Figure 19 shows the cost-effectiveness of the considered desiccants, considering a solution temperature of 25 °C. As shown in the figure, salts with a lower price results in a higher cost-effectiveness. The high difference in cost between the better and the less performing desiccant solutions is a parameter that should be carefully considered in the evaluation of the total cost of LDAC system. When the dehumidification performance is a factor of not primary importance, cheaper solutions are always the proper choice. $CaCl_2$ solution shows the highest cost-effectiveness, followed by HCO_2K desiccant solution. Even if with higher dehumidification ability, the high cost of LiCl and LiBr solutions makes them less interesting from an economic point of view.

As described in Section 3.4, the thermo-chemical energy storage with liquid desiccants is a very promising technology that could allow to perfectly match available heat sources with dehumidification/cooling demands. Table 8 is given to show the comparison of the costs of the different thermal energy storage technologies per kWh delivered [113]. It can be seen that the thermo-chemical

storage cost is higher than the other technology, this is mostly because this technology is still in the R&D phase. However, the thermo-chemical storage with liquid desiccant is almost free-losses. Therefore, the possible transport of liquid desiccant over short and medium distances and use in hybrid district networks must be accounted to evaluate of the possible economic savings resulting from the employment of the thermo-chemical storage technology [142].

Table 8 Cost of the main energy storage technologies [113, modified].

Thermal Energy Storage Technology	Cost [GBP/kWh]
Sensible Storage (Water)	0.079-10.22
Latent Storage (Phase-Change Material)	10.22-51.12
Thermo-Chemical Storage (Thermo-Chemical Fluid)	7.86-102.24

The cost of the desiccant solution plays a key role in the determination of the best performing desiccant solution for storage [41]. Table 9 shows the cost for storing latent cooling with different desiccant solutions under the conditions given in Figure 18 and Table 7. Due to the loss-free nature of the storage, the cost of the storage tank can be sensibly reduced, using a less expensive material, such as uninsulated plastic, resulting in economic savings respect the cost of tanks for hot water sensible storage [41]. Nevertheless, the table shows how the storage cost is highly influenced by the cost of the desiccant. This high cost limits the use of expensive desiccants for storage, such as LiCl and LiBr solution, particularly for long-term storage.

Table 9. Cost of liquid desiccant storage

Salt	Storage capacity [GBP/kWh]	Density [kg/m^3]	Volumetric storage cost [GBP/m^3]	Energy storage cost [GBP/kWh]
LiCl	228.725	2,070	13,417.78	58.66

CaCl$_2$	248.52	2,150	482.17	1.94
LiBr	214.14	3,460	8,835.11	41.26
MgCl$_2$	298.34	2,320	1,288.33	4.32
HCO$_2$K	160.74	1,908	550.17	3.42

5. Application and climatic condition

For a complete understanding of the overall performance of LDAC systems, other factors should be considered, such as the application of the liquid desiccant technology and the climatic conditions where the machine is used. As a matter of fact, these factors play a key role in the determination of the system performance. It should be mentioned that no desiccant is best for all the applications and climatic conditions.

5.1 Different applications

As previously described, one of the primary advantages of LDAC technology coupled with sensible cooling (vapour-compression, absorption or evaporative cooling) is its capacity to separately treat temperature and humidity, e.g. the sensible and latent loads [3]. As a matter of fact, conventional electrically-driven chillers result highly inefficient in dealing with latent loads from the energetic point of view. This is due to its moisture removal process, based on cooling until the dew-point, overcooling and moisture removal by condensation and reheating until the desired supply air conditions. On the other hand, the separate handling of sensible and latent loads performed by integrated LDAC system results in the reduction of the system size and energy consumption.

The majority application of integrated LDAC systems is for buildings [1]. The sensible heat ratio, SHR, of the building load is believed to be a critical factor for the determination of the energy consumption of air-conditioning systems. As a matter of fact, the SHR of the building load and of the air-conditioning system must match in order for the air-conditioning system to efficiently deal with both sensible and latent loads present in the building [2]. The SHR of the building can be calculated as [143]:

$$SHR = \frac{Q_{sensible}}{Q_{sensible}+Q_{latent}} \tag{13}$$

where $Q_{sensible}$ and Q_{latent} represent the sensible and latent load of the building, respectively.

Following the ASHRAE standard 90 [8], a better energy efficiency of the building was obtained starting from the 1980s with the employment of fluorescent energy-efficient lighting, reduced window U-values, better insulation of walls and roofs, low-energy glasses, CFD-LED lights, white roofs, etc. [37, 144]. On the other hand, latent loads mostly due to ventilation air remained almost constant in the same period. In fact, following the ASHRAE Standard 62.1 [7] there is a minimum value of the outdoor air delivered to buildings to ensure thermal comfort and indoor air quality, resulting in a higher productivity in the workplace [37]. This shifts toward low-SHR systems has led to a higher importance for HVAC systems in dealing with humidity and latent load, making the conventional electrically-driven vapour-compression system a technology highly inefficient in humid climates or in working environments when the humidity control is crucial. For buildings characterised by SHR lower than 75 %, conventional air-conditioning systems struggle in dealing with latent loads [1].

Different markets could benefit from different applications of LDAC system. The technology has been applied to different sectors, such as residential and commercial buildings and industrial sector [145-147], some examples are summarised below:

(1) The humidity control of conventional vapour-compression cooling systems in hot and humid climates is highly energy inefficient. These systems fail to exactly match the required humidity value most of the time. In such climate, LDAC technology is the best available technology for humidity control.

(2) Buildings with a high latent load, such as pools, have been identified as a very promising application for LDAC technology [144, 148]. In this case, the pool water can be used to remove the heat of absorption resulting from the dehumidification process with beneficial effect in terms of reducing heating water pool consumption [149].

(3) LDAC could also fit to the application that require high and stringent control on humidity for the conservation of the good or for production requirements, such as industrial drying, food processing

and preservation, painting process, greenhouses, etc. A technology able to ensure an exact value of humidity will result in an increase product quality for these sectors [22]. Depending on the air humidity content required by different processes, different desiccant solutions result the most performing from a cost-effectiveness point of view. The application of LDAC technology for refrigeration application in food and beverage industry, such as breweries, meat cooling, etc., is a novel subject under study [146].

(4) Beside dehumidification, LDAC system can also be used to provide cooling by conducting evaporative cooling with the produced dry air. The system has been proved to perform well in some demonstrated application cases, providing cooling for the refrigerant space or reducing the condensation-related problem, such as frost. Moreover, LDAC cooling systems do not require defrost system, resulting in an economic saving [146, 149].

(5) Greenhouses require a control on the relative humidity for the optimal growing condition of plants, the relative humidity required for greenhouse application is higher than residential air-conditioning. As an example, tomatoes and cucumbers require a relative humidity of 80-85% to grow with a temperature of 27-29 °C [17]. Therefore the powerful dehumidification process is not necessarily required by these greenhouses, while cheaper LDAC technologies using cheap liquid desiccant solutions with a higher equilibrium relative humidity, such as $MgCl_2$, $CaCl_2$, and HCO_2K solutions, could be more performing from a cost-effectiveness viewpoint. Davies et al. [17] investigated the use of seawater bitterns in LDAC systems for greenhouse application.

Depending on the level of the humidity control and on the temperature range required by the process, the most appropriate desiccant solutions are different from a performance and cost point of view. As described in Section 3.5.2, the use of halide salt solutions gives rise to the corrosion phenomenon, which becomes more evident as the temperature increase. Therefore, no chlorine or bromine desiccant solutions must be employed for high-temperature recovery applications. Pineda Quijanoa et al. [150] showed the feasibility of a LDAC system using phosphoric acid (H_2PO_3) as liquid desiccant to produce hot and dry

air for milk powder drying process, while the temperature reached by the desiccant solution in the cycle does not allow the utilization of common desiccants.

5.2 Different climatic conditions

The energy consumption and performance of LDAC systems in buildings is highly influenced by the climatic conditions. Ronghui et al. [151] compared the performance of LDAC system in different climatic conditions. Results indicated that the optimization process of the system is strictly related to the climatic conditions. As predictable, the best performances were obtained with hot and humid climates. The influence of the climatic conditions on the performance of LDAC system is shown in Figure 18. In the figure, the moisture content of ambient air in six different climatic conditions (listed in Table 9) and the vapour pressure of different desiccant solutions at 25 °C with different concentration values until saturation are shown. Table 9 reports the mass fraction value at which the equilibrium moisture content of the solution equilibrates the absolute humidity of the ambient air. In the Figure 20, the dehumidification process begins when the desiccant solution has a mass fraction higher than these minimum values, which are dependent on climatic conditions.
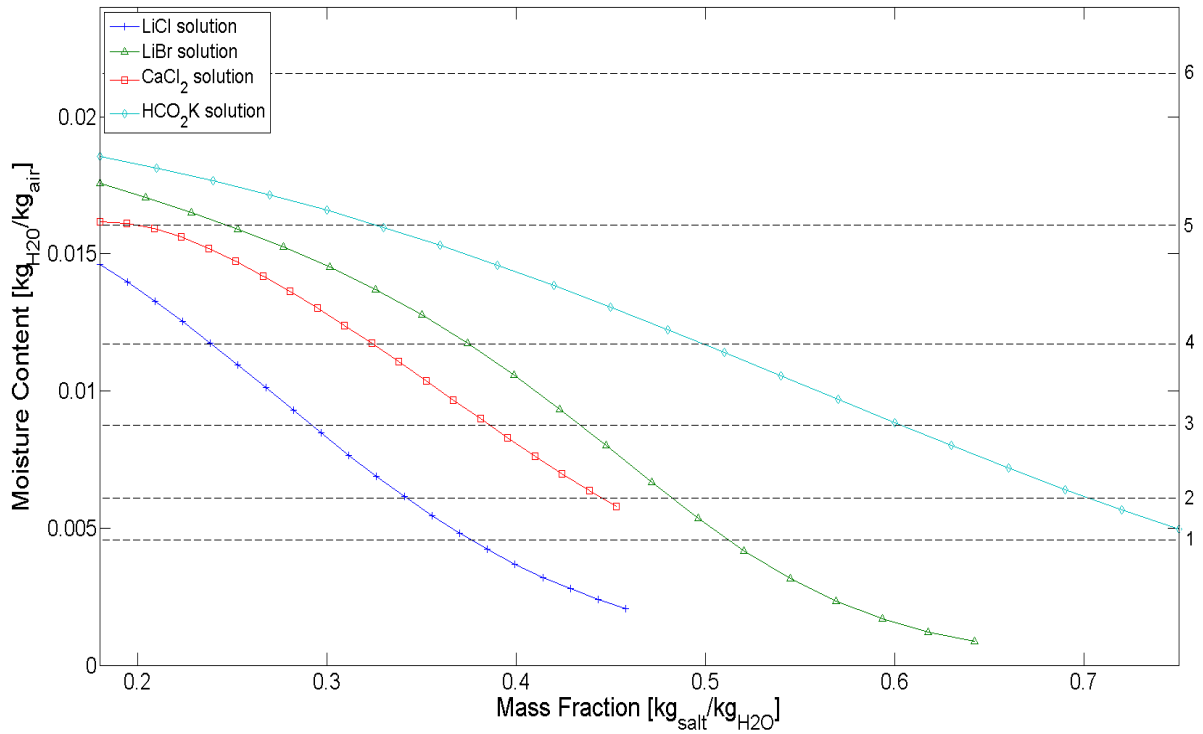
Figure 20 Dehumidification ability of desiccant solutions in different climatic conditions, the climatic conditions representing by dash lines are given in Table 9.

Table 10 Minimum mass fraction required by desiccants for dehumidification under different climatic conditions.

Climatic condition			Minimum mass fraction for dehumidification			
	Temperature [°C]	RH [%]	LiCl	LiBr	CaCl$_2$	HCO$_2$K
1	10	60	0.3766	0.5113	N/A	N/A
2	10	80	0.3429	0.4833	0.4447	0.7039
3	20	60	0.2923	0.4133	0.3868	0.6061
4	20	80	0.239	0.376	0.3234	0.502
5	30	60	0.1439	0.25	0.2048	0.3297
6	30	80	All	All	All	All

Table 10 shows how the ambient condition strongly influences the dehumidification process. In a cold and relatively humid condition, such as Case 1, only LiCl and LiBr can perform the dehumidification process. In this condition, the difference between the equilibrium vapour pressure of these solutions and the partial vapour pressure of the air is small, therefore the moisture removal process is less-efficient. On the other hand, LDAC systems are progressively more able to efficiently dehumidify the ambient air in hotter and more humid climates. For a particularly hot and humid climate, all the considered desiccant solutions are able to effectively perform the dehumidification process (Case 6). Consequently, the air ambient condition is a critical factor for the determination of the optimal desiccant for air-conditioning. In hot and humid climates, cheap less-performing could be utilised for dehumidification, while desiccant solutions with higher dehumidification ability are needed as the ambient temperature and humidity decrease.

6. Innovative liquid desiccants

The paper has shown that the satisfaction of all the desirable properties of an ideal desiccant is impossible. For this reason, the research led to the evaluation of alternative solutions employable as working fluid to overcome the common drawbacks of common desiccants, such as corrosion, crystallization, and high cost-effectiveness. Novel alternative desiccants were studied, such as bio-desiccants, composite desiccants and polymeric desiccants [152-154]. Meggers et al. [154] used an advanced desiccant solution composed of 70-90 wt% alkoxylated siloxane mixture, with the remaining 10-30 wt% of polyol. The feasibility of this solution in LDAC systems integrated with a façade in humid climates was proved.

A promising alternative is the employment of ionic liquids (ILs) as working fluids in LDAC systems [26, 27, 91]. ILs are salts that remain liquid at ambient temperature, usually composed by an organic cation and inorganic anion. These fluids, characterised by their unique properties of high thermal and chemical stability, high electrical conductivity, and very low vapour pressure, find application in many research and industrial fields, such as replacement for green solvents, electrochemical batteries, treatment of nuclear waste, etc. [155-157]. Moreover, the fluidity of ILs over LDAC working temperature range

addresses the crystallization problem. One of the most interesting aspects of ILs is their flexibility. In fact, their properties can be tuned depending on the desired application by adjusting the cation and/or the anion, therefore leaving the opportunity for the research and development of a fluid capable of behaving as close as possible to the ideal desiccant conditions, enabling different temperature and concentration operating conditions not allowed by common desiccants. Therefore, an ideal fluid for LDAC systems, characterised by the respect of health and safety, non-corrosive, non-volatile, low equilibrium vapour pressure, low density and viscosity, high specific heat capacity, high thermal conductivity, high diffusion coefficient of water vapour in the desiccant could potentially be reached by a tailor-made IL.

The use of these solutions as a replacement in absorption chillers and absorption heat pumps has been investigated in the past [155, 158]. In the last period, the use of ionic liquids in a membrane contactor for cooling and dehumidification has been investigated [159-162]. Chugh et al. [160] investigated the use of ionic liquids as working fluid in a combined water heater, dehumidifier, and cooler. The thermodynamic properties of vapour pressure, density, viscosity, thermal conductivity, heat of absorption, mass diffusion coefficient, and corrosion rate for five different ionic liquids have been investigated. Some of the investigated ionic liquids showed a good behaviour for use in LDAC systems. The only shown deficiency is the low mass diffusion coefficient of water in these solutions that lowers the absorption/desorption rate in the dehumidifier/regenerator. The technological solution to resolve this problem is the realisation of a chaotic mixing of the solution flow obtained through surface microstructures able to create vortices [161]. Between all the possible combinations of ILs (10^{18} possible combinations), the imidazolium-based ILs are considered as the most interesting one for LDAC application [27]. Huddleston et al. [162] showed how for imidazole-based ILs the hydrophilicity/hydrophobicity of the solution is affected by the choice of the anion. Luo et al. [27] observed how the length of alkyl chain in the IL can determine the equilibrium vapour pressure of the IL. The current research on the best performing ILs for LDAC technology showed the ability of fluids characterised by shorter alkyl chain and imidazole cation, such as 1-3-dimethyl-imidazole [DMIM] and 1-ethyl-3-methyl-imidazole [EMIM], and soluble anion, such as acetate, chlorine, bromine, iodine, etc. group. The possible corrosion to metals for ILs composed by acetate, chlorine,

bromine, etc. group for high-temperature applications requires further studies to be done to evaluate their corrosion rate to metals [156].

The dehumidification potential of ionic liquids for LDAC systems has been investigated in the past [26, 27, 157]. Luo et al. [26, 27] numerically and experimentally investigated the dehumidification performance of [EMIM][BF₄], [DMIM][OAc], [BMIM][BF₄] solutions. Qu et al. [157] investigated the thermodynamic properties of a [EMIM][OAc] aqueous solution using the e-NRTL model based on the Prausnitz's formulation [164]. As shown in Figure 21, the dehumidification potential of a 91.77 % wt. [DMIM][OAc] and of a 70 % wt. [EMIM][OAc] solution is similar that of a 40 % wt. LiCl solution [27, 157]. This result shows the dehumidification potential of some ILs and how the possible employment of these in LDAC systems could result very interesting.
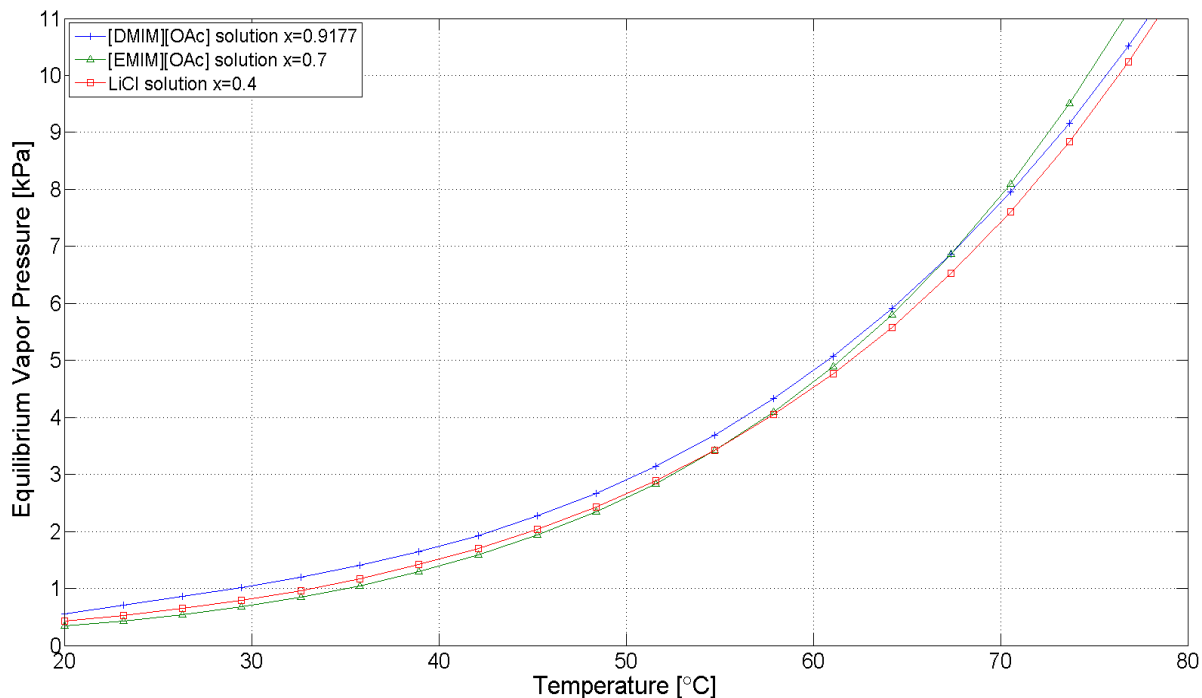

Figure 21 Equilibrium vapour pressure of LiCl, [DMIM] [OAc], [EMIM][OAc] solutions [27, 157].

Nowadays, the cost of ILs is too high to make these fluids interesting from an economic viewpoint to justify their widespread use. The current price of ILs employable in LDAC systems is shown in Table 11 [165-167]. However, these fluids are still in the R&D phase, therefore a possible meaningful reduction of the cost should be obtained with an industrial utilization of these fluids.

Table 11 Price per kg of ILs.

Ionic Liquid	Price per kg (GBP)
[EMIM][OAc]	627
[BMIM][BF$_4$]	1554
[EMIM][BF$_4$]	6980
[DMIM][OAc]	N/A

In addition to that, the use of a solution less likely to crystallize and corrode metals can result in an overall reduction of the system cost, both of the primary (use of cheaper metals) and operational cost (reduced maintenance, etc.). Therefore, the interesting opportunity derived from the employment of ILs in LDAC systems makes this research field worth of additional insight. Apart from thermodynamic and economic properties, other questions must be addressed in the evaluation process of alternative innovative fluids as liquid desiccant for HVAC application. In fact, the possible reaction with contaminants present in the air, biological growth, and odours created by the alternative solution must be studied before using the fluid for air-conditioning applications [87]. Considering the need for the future development of refrigerants not responsible for the greenhouse effect, these fluids result very promising for a wide range of applications and must be further studied and developed in the next period.

7. Conclusion

Liquid desiccant air-conditiong systems are becoming a widespread energy-efficient environmentally friendly dehumidification/cooling technology. The liquid desiccant systems present multifunctional

properties that make them particularly interesting in several fields of application. The main fluids employed as liquid desiccant have been reviewed and investigated. The thermodynamic properties involved in the choice of the use of these as liquid desiccants have been thoroughly described. There is not a 'one-size fits all' desiccant solution for all the working, climatic and applicative conditions. The impact of the different solutions on the related process has been clarified to understand which solutions are employable in these systems and why. The conclusions are summarised below:

(1)   The dehumidification ability of a desiccant solution is related to its equilibrium vapour pressure, namely the vapour pressure of water molecules on the surface of the solution in contact with the air. The lower the equilibrium vapour pressure, the higher the ability of the system to reach dry conditions for the processed air. LiCl and LiBr solutions show the higher dehumidification ability. The equilibrium vapour pressure of desiccant solutions shows direct proportionality with temperature and inverse proportionality with mass fraction. Any crystallization of the liquid desiccant solution must be strictly avoided to not degrade the system's performance and increase its maintenance cost.

(2)   The electric consumption of liquid desiccant air-conditioning systems is significantly lower than vapour-compression systems. The density, dynamic viscosity, and moisture absorption rate of the different desiccant solution influence the electric consumption for fans and pumps in the system. LiCl solution shows the lower electric consumption.

(3)   Other thermodynamic properties, such as specific heat capacity, diffusion coefficient, etc. have an impact on the performance of the system, influencing the heat and mass transfer in the air/solution contact. The enhancement of the heat and mass transfer is a primary research in the liquid desiccant air-conditioning field. Possible solutions have been identified in the realization of internally-cooled dehumidifiers, innovative packing materials or design, etc.

(4)   Primary requirements for their employment in heating, ventilation and air-conditioning is the respect of health and safety requirements. The LD50 is used to evaluate the toxicity of desiccant solutions. Even if not particularly high of the desiccant toxicity, any carry-over of desiccant solution must strictly be avoided for building applications.

(5)   Thermo-chemical energy storage is a very promising opportunity for liquid desiccant systems. The storage with liquid desiccants is almost free-losses and characterised by higher energy density comparing to sensible and latent thermal energy storage technologies. These characteristic makes the liquid desiccants employable as working fluid alternative in district dehumidification/cooling/heating networks. The energy storage capacity is primarily a function of the operative conditions of the system and secondarily on the equilibrium vapour pressure and density of the solution. $MgCl_2$ solution shows the best behaviour for thermo-chemical storage.

(6)   The price of desiccant used in the system largely influences the overall cost of the system. The desiccants able to ensure a better dehumidification, e.g. LiCl and LiBr solutions, are expensive; on the other hand, $MgCl_2$ and $CaCl_2$ solutions are able to dehumidify the air to a less extent but they are very cheap because mostly produced by seawater or industrial processes. The price of HCO_2K makes it interesting for employment in LDAC systems. Analysing the problem from a cost-effectiveness viewpoint, $MgCl_2$, $CaCl_2$, and HCO_2K solutions are able to reach the best dehumidification while having the lowest price. For the thermo-chemical storage with desiccant solutions, the cost of the solution plays a primary role. Storage with expensive desiccants, such as LiBr and LiCl, is extremely unfeasible from an economic point of view, particularly for long-term storage.

(7)   For high-temperature application, the use of halide salt solutions gives rise to corrosion. The alternative use of desiccants less responsible for corrosion such as HCO_2K, $Ca(NO_3)_2$, and H_2PO_3 solutions were studied and considered feasible.

(8)   The ambient climatic conditions is another key factor for liquid desiccants. The energy consumption and economic performance of the system is strictly related to the outdoor air conditions. For hot and humid climates, it is possible to perform the dehumidification process with all the desiccants considered under every mass fraction value. As the temperature and humidity of the outdoor air decreases, more expensive and better performing desiccant solutions, such as LiCl and LiBr are needed.

(9)   This overview is intended to be a starting point in the determination of viable alternatives respect halide salts solutions as working fluid, able to overcome their main drawbacks, such as corrosion and

crystallization issues. Towards this direction, ionic liquids seem to be a promising solution. Their employment in absorption technologies has been largely described in the past and seems feasible in liquid desiccant air-conditioning systems. The characteristics of low-vapour pressure, low density and viscosity, high solubility and non-corrosion to metals make this fluid an important and promising candidate for employment in the system that needs to be further investigated to get the best out of LDAC technology. The dehumidification ability of imidazole-based ILs, such as [DMIM][OAc] and [EMIM][OAc], was shown. Further research needs to be conducted for a complete understanding of the behaviour of these promising fluids for liquid desiccant application.

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