A Physicochemical Study of Cost-Effective Liquid Desiccants for Use in an air conditioning systems

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Abstract: Liquid desiccant systems (LDS) have attracted attention as promising low-energy alternative cooling solutions relative to conventional systems. An integral part of the LDS dehumidification capability depends on the composition of the hygroscopic desiccants utilized. The vapour pressure of different hygroscopic salt solutions and mixtures thereof have been measured at a temperature of 298.15K using a Yamamoto configuration. The initial validation of the measurement configuration using a single salt solution has exhibited a satisfactory correlation with vapour pressures reported by previous authors at various concentrations. The performance of $MgCl_2$ solution was found to be comparable to that of LiCl. The results have shown that $MgCl_2$ solution with 30% w/v concentration is sufficient to maintain the equilibrium relative humidity (ERH) at 50%, the recommended value for the human comfort zone, a value close to that obtained from LiCl solution (ERH = 55%) with the same concentration. Moreover, the best performing salt solution mixtures were found to be magnesium and lithium chlorides. Considering that the cost of LiCl is 23 times higher than that of $MgCl_2$, the potential replacement of LiCl with $MgCl_2$ in LDS is very promising from both a performance and cost point of view. The concentrated seawater brines have also shown a very promising performance comparable with that of 50% $CaCl_2$– 50% $MgCl_2$ artificial mixture.

Keywords: Low energy cooling, liquid desiccant systems, hygroscopic salt solutions.

1. INTRODUCTION

An ambitious worldwide commitment supports the radical cuts in greenhouse gas emissions as highlighted by the intergovernmental panel on climate change's fifth assessment report (IPCC AR5) [1] with the intention to set out a pathway for achieving deep emission cuts by the midpoint of the century. Energy efficiency has been identified to be a key driver of the transition, and the built environment is expected to provide low-cost and short-term opportunities to reduce emissions; first and foremost, through the improvement of the energy performance of buildings. The built environment accounts for about 40% of global anthropogenic energy consumption of which, in hot climates, 60% goes to space cooling [2]. Among several technologies, hybrid evaporation and direct expansion (DX) based technologies show promising potential for energy saving [3]. However, in more humid climates, dehumidification stage in hybrid systems is in particular needed for further energy consumption reduction.

Desiccant cooling with dehumidification systems (DCS) are technologies that may overcome the challenges in hot high humid climates. Although the principle of desiccants has been known for some time, the use of DCS for air conditioning systems have increased significantly over the past several years[4]. DCS have been proposed as viable alternatives to conventional cooling systems, such as vapour compression refrigeration systems, resulting in a substantial reduction in energy consumption [4,5]. Desiccant utilization technologies are distinguished in the literature as solid or liquid desiccant systems according to the state in which the desiccant is found. Both have shown excellent potential in reducing the energy consumption of conventional cooling systems, but each suffers from some drawbacks which need to be considered. Solid desiccant systems (SDS) are the systems in which the desiccant is presented in its solid-state, and they are generally Used in industry with key examples including zeolites, molecular sieves.

SDS are generally capable of achieving high drying rates of air streams and can operate in varying pressure environments [6]. In the liquid desiccant systems (LDS), the desiccants are specific chemicals that can capture moisture from humid air. They provide a level of vapour pressure lower than water displays at the same temperature, allowing air that moves through this lower pressure solution to become dehumidified [7]. Depending on the concentration and temperature, liquid desiccants can also achieve equilibrium with air at a fixed humidity level [8]. Moreover, liquid desiccant systems (LDS) require much lower regeneration temperatures than SDS and allow highly efficient heat recovery by the transfer between concentrated and dilute desiccant containing solutions in heat exchanger configurations [9].

The chemicals used in the liquid desiccant systems might be organic or inorganic compounds. The inorganic-based desiccants generally consist of inorganic salts dissolved in aqueous solutions with low vapour pressure potentials. Lithium chloride is an example of the most commonly used inorganic salt for absorption in dehumidification systems. Although liquid desiccant systems substantially reduce the energy requirement for space cooling and dehumidification, there is a general preference for conventional solutions at the cost of higher energy consumption [5]. However, some of the main disadvantages of LDS is the high corrosivity and the potential of crystallisation at high mass fractions and low temperature. Some inorganic salts can cause damage in some metallic parts of the desiccant system. [6]. Therefore, more studies are still needed, towards the development of efficient and sustainable solutions for dehumidification and cooling in industrial, commercial and residential environments. Many authors have conducted studies of salt solution vapour pressures, densities and heat capacities. Although the physicochemical and thermodynamic properties of organic liquid desiccants are well

documented in the industry as well as in academia [10,11], inorganic salts are still less covered.

Regarding the vapour pressures of different concentrated salt solutions, there is a wide spectrum of data reported throughout literature. Patil et al. [10] investigated the vapour pressures among other properties of salt solutions to ascertain the feasibility for their use in various industrial applications such as desalination process. The authors studied the vapour pressures of LiCl, LiBr and LiI aqueous solutions at different salts' concentrations and temperatures. Researchers [10] also continued their studies by investigating the potential of alternative inorganic salts known to have lower dehumidification potentials[1] than those of the lithium salts in the previous study. The salt solutions were studied at five different temperatures ranging between 303.15 K and 343.15 K and were correlated against the Antoine equation [11]. It was concluded, based on the activity coefficients produced by the measured vapour pressures of the salt solutions, that the salt solutions exhibited non-ideal behaviour for dehumidification.

Chung and Luo [11] made initial progress to study the vapour pressure of dissolved inorganic salts in solutions with the purpose of relating them to their effectiveness as liquid desiccant dehumidifiers. They followed the vapour pressures of salt solutions containing one of LiCl, LiBr and $CaCl_2$ in concentrations ranging from 35 to 45 % w/v (g of solute/100 mL of solution). The vapour pressures were followed at temperatures ranging from ambient 298.15 K to 313.15 K. The apparatus used to correlate vapour pressures of salt solutions against dehumidification effectiveness utilized a modified version of an equipment configuration developed by Yamamoto et al. [12] to measure the solubility of helium in liquids. They calculated the effectiveness of dehumidification by following the humidity of the inlet and outlet air streams passing through the salt solution-containing apparatus.

Chen et al. [13] studied the vapour pressures using the modified Yamamoto configuration developed by Chung and Luo [11], as well as densities of salt solutions mixtures consisting of water + (50-80%) organic desiccant + (4-25%) inorganic salt. The inorganic salts chosen were lithium chloride and lithium bromide, and the chosen organic desiccant compounds included: tetraethylene glycol, diethylene glycol and dipropylene glycol. The parameters were investigated at temperatures ranging from 303.15K to 343.15K. Chen et al. [9] concluded that the addition of inorganic salts did, in fact, yield lower vapour pressures and thus could be used to improve the effectiveness of a desiccant cooling system. The densities measured were shown to be in line with those previously reported in other literature [15,16]. The same research group continued their investigations using the same experimental configuration, for the study of density and vapour pressure of mixed salt solutions, where magnesium chloride replaced the previously used lithium salts. In these investigations, a fixed 40% concentration of one of diethylene, triethylene or tetraethylene glycol was used in all experiments with three concentration points (in wt. %) of interest chosen for magnesium chloride: 4, 9 and 16. The tests were conducted at temperatures ranging from ambient 293.15K up to 343.15K. The authors reported vapour pressures significantly higher than their previous work, confirming the lower affectivity of $MgCl_2$ relative to LiCl.

In a bid to consolidate the gap between dehumidification capabilities of lithium salts and alternative counterparts such as $CaCl_2$, Ertas et al.[16] investigated the possibility of using salt solution mixtures: termed "cost-effective liquid desiccants"

(CELDs). They observed that a CELD mixture of LiCl and $CaCl_2$ solution significantly improved on the vapour pressures achieved by calcium chloride single salt solutions. This posed the possibility of salt solutions with promising dehumidification potentials at a 30% lower cost relative to a lithium chloride single salt solution.

Energy consumption reduction in the built environment in hot and humid environments is largely untapped, partly due to the lack of fundamental research related to alternative dehumidification solutions in hybrid systems. The data produced by reporting authors are of great value to the development of a database to supply model calculations. However, the collation of a complete database, to produce a calculation model in order to predict the effectiveness of a salt solution mixture in a dehumidification and cooling system at varying conditions, requires further study to fill the gaps in the reported literature. A full analysis and tabulation of the physicochemical properties would be investigated herein to understand the effect of using varying mixtures of dissolved salt solutions.

2. Materials and Methods

1. Materials

The vapour pressure data for the liquid desiccants used in this study were determined using single salts as well as salt mixtures dissolved in aqueous solutions. Magnesium chloride (crystals), lithium chloride (anhydrous) and calcium chloride (dihydrate) were manufactured by ALPHA CHEMIKA (India) with purity 90 %, 99%, 98% respectively; and the ternary system containing: $MgCl_2$ + LiCl + water, $MgCl_2$ + $CaCl_2$ + water. Distilled water has been manufactured by QNAF (Qatar). The water content of the salt samples has been taken into consideration when preparing the solution concentrations. Also, concentrated seawater was analysed for its dehumidification potential.

2. Procedure for Vapour Pressure Measurement

To obtain the necessary vapour pressure data, a simple experimental configuration was constructed by which the relative humidity of the local atmosphere above the salt solution samples could be monitored. In each experiment, 100 ml of different concentrations of salt solution were placed separately in a closed system (using glass desiccators as shown in Fig. 1) to obtain the equilibrium relative humidity (ERH), and subsequently calculate the equilibrium water vapour pressure P_v from equation 4. The salt solution samples were placed inside a desiccator which was immersed in a temperature-controlled water bath using a VacMaster unit (a Sous Vide immersion circulator) manufactured by ARY, Inc. All studies were conducted in water baths controlled at 298.15K to avoid any variation in the recorded relative humidity. The humidities and temperatures were then continuously measured in the sealed system using Rotronic HygroPalm HP22 inserted into the desiccator.

The HP22 measures conditions within the range of 0 to 100% RH and -100 to 200°C at a data refresh rate every second. The humidity reference value was ±0.8%, and the experimental error of temperature measurements was estimated to be ±0.1 K. The accuracy and precision of this system configuration was first validated against reported literature data for single salt solutions before being applied to new mixtures to be studied, as shown in table 1. Each result measurement was repeated at least five times to ensure the accuracy of the system.

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[1] The capability for a desiccant to remove moisture from its local atmosphere [20].

Fig. 2. Indicative curve to illustrate equilibrium relative humidity of salt solution

Fig. 1. The measurement of ERH of salt solution (a) Actual experimental set-up (b) Schematic diagram.

After stabilization of the RH was reached, the experimental set up was left for a duration of at least 3 hours as shown in Fig. 2 and was recorded as ERH. The delay to achieve the ERH inside the desiccator was due to the small surface area of the salt solution relative to the local atmosphere around the sample. This stabilized value of RH was then recorded as the ERH which was employed to calculate the water vapour pressure using equation (4). This equation was obtained from the empirical equation introduced by Alduchov et al. [17] (equation (1)) from which the saturation vapour pressure of pure water over a plane surface of the water at a fixed temperature was calculated,

$$P_g = 6.112 \times e^{\left(\frac{17.67 \times T}{T+243.5}\right)} \tag{1}$$

Since the relative humidity is commonly defined as the ratio of the actual water vapour pressure to the saturation pressure at the same temperature as shown in equation (2) below [17]:

$$\text{ERH} = \frac{P_v}{P_g} \tag{2}$$

Thus, the saturation pressure can be calculated by rearranging equation (2) to give equation (3):

$$P_g = \frac{P_v}{\text{ERH}} \tag{3}$$

Consequently, from equation (1) and (3) the vapour pressure as a function of relative humidity and temperature can be calculated as Shown in equation (4) below:

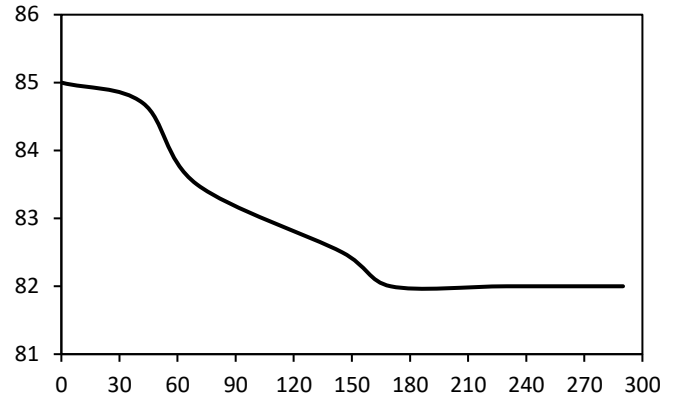$$P_v = 6.112 \times \text{ERH} \times e^{\left(\frac{17.67 \times T}{T+243.5}\right)} \tag{4}$$

3. Results and Discussion

Initially, the single salt solutions including $CaCl_2$, $MgCl_2$ and LiCl were mainly utilized for the validation of the experimental setup. Thus, the data were plotted and compared with reporting authors who conducted single salt solution experiments at similar conditions as shown in Fig.s 3, 4 and 5.

Fig. 3 presents the result of the ERH measurements obtained by using aqueous solutions of $CaCl_2$ with concentrations varying from 15 % w/v to 40 % w/v, as compared to those obtained by Patil et al.[10] and DOW [18] for similar $CaCl_2$ solutions at the same temperature of 298.15 K. Similarly, Fig. 4 shows the ERH of $MgCl_2$ solutions with concentrations varying from 15 % w/v to 36 % w/v $MgCl_2$ in comparison with values obtained by Patil et al.[10] and Lychnos et al. [19]. The results of LiCl solutions compared to those obtained from the study of Patil et al. [10] are shown in Fig. 5.
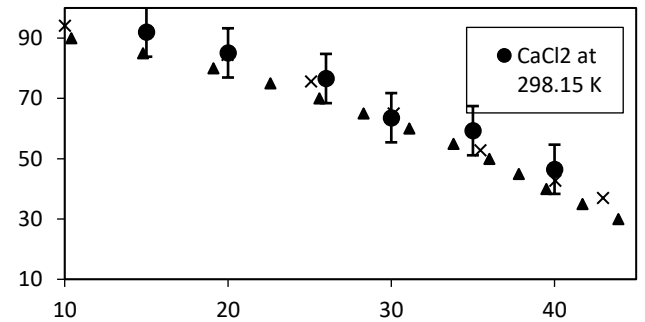

Fig. 3. Comparison of the measured equilibrium relative humidities of $CaCl_2$ salt solutions with the data reported in the literature [10, 11] (with a ±8.9% error margin).
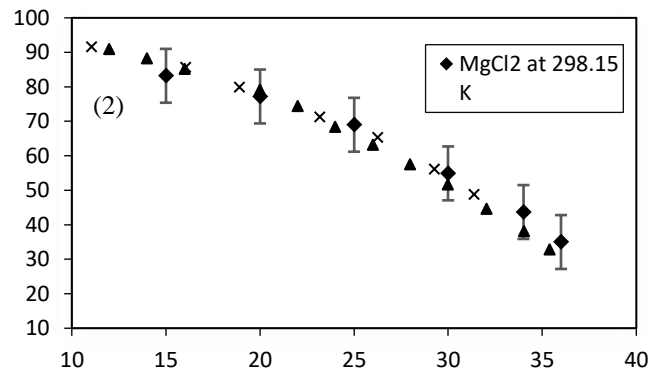

Fig. 4. Comparison of the measured equilibrium relative humidities of $MgCl_2$ salt solutions with the data reported in the literature [11, 20] (with a ±7.8% error margin).
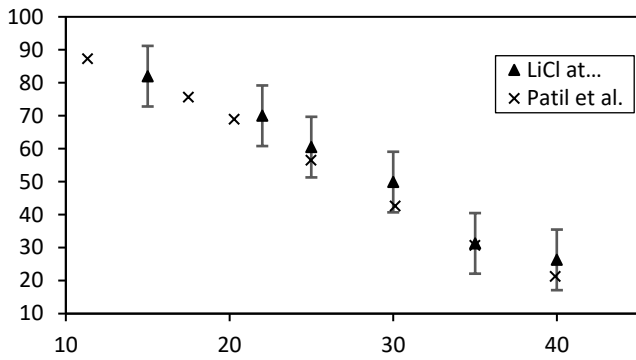
Fig. 5. Comparison of the measured equilibrium relative humidities of LiCl salt solutions with the data reported in the literature (Patil et al. 1991) [10] (with a ±9.2% error margin).

As depicted in Fig. 6, the ERH analysis of the single salt solutions showed that $MgCl_2$ solutions provided comparable values relative to that of LiCl; which is known as an effective desiccant [10]. On the other hand, the $CaCl_2$ salt solutions required higher concentrations to achieve the same levels of ERH values achieved by the $MgCl_2$ solutions at lower concentrations. For example, to reach 50% of ERH, a $MgCl_2$ solution of 34% w/v concentration was sufficient whereas 40%w/v concentrated solution of $CaCl_2$ was required to reach the same performance. These experiments, in turn, showed promising results for the utilization of seawater brines (due to its significant Mg content when concentrated) as a potential liquid desiccant in cooling systems.
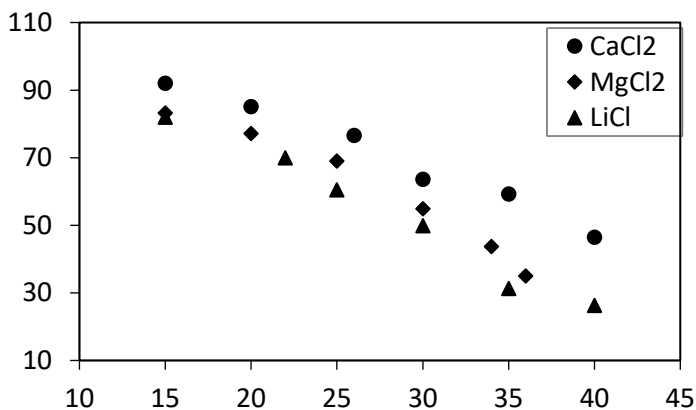

Fig. 6. Comparison of the measured equilibrium relative humidities of single salt solutions.

Comparison of the measured ERH of single salt solutions clearly showed a similarity of the experimental results to those reported in the literature; thus, clearly validating the modified experimental set-up.

For a given concentration of solutions used in this study (Table 1), the vapour pressure (P_v) inside the desiccator was calculated by substituting the associated ERH and various temperatures (T) into equation four as shown in Fig.s 7 and 8.

To achieve a balance between dehumidification performance and economic viability, it is worth testing the performance of mixed solutes solutions. Because the $MgCl_2$ showed promising vapour pressure reduction, mixtures containing $CaCl_2$ and $MgCl_2$ were investigated for their vapour pressures. Salt solutions consisting of 50% $MgCl_2$ and 50% $CaCl_2$ were prepared in an aqueous solution with a total solute concentration of 35% to mirror the studies conducted by Ertas et al. (Fig. 7). In their study, Ertas et al. [16] investigated the performance of mixed solute solutions containing $CaCl_2$ and LiCl, naming the optimal mixture as a "cost-effective liquid desiccant (CELD)". The 50/50 35% w/v

mixture achieved the best ERH values thus improving substantially on the vapour pressure reduction achieved by using $CaCl_2$ single salt solutions.
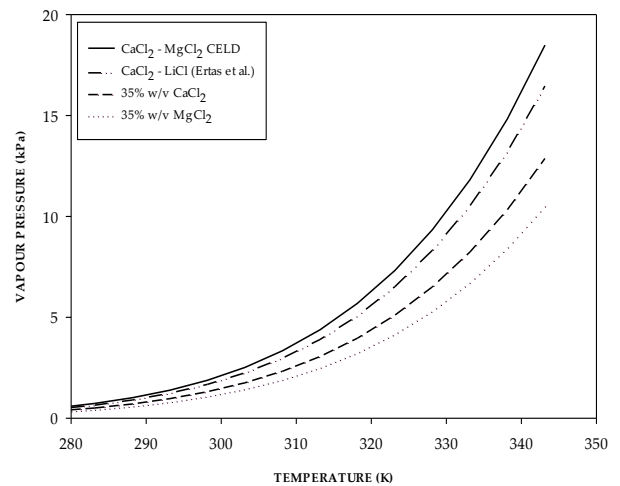

Fig. 7. Comparison of the vapour pressures obtained of 35 % w/v $CaCl_2$-$MgCl_2$ CELD mixture against the 35% w/v $CaCl_2$-LiCl CELD mixture reported by Ertas et al. [16]; in addition to the data obtained from the $MgCl_2$ and $CaCl_2$ single salt solutions.

As expected, the $CaCl_2$-$MgCl_2$ CELD mixture did not achieve vapour pressure reductions to a level relative to the mixtures studied by Ertas et al. [16]. However, there was certainly an improvement on the vapour pressure reduction relative to the $CaCl_2$ salt solution. It is clear that a mixture including LiCl and $MgCl_2$ would substantially improve on the CELD values achieved by Ertas et al. Nevertheless, $CaCl_2$ and $MgCl_2$ would serve as a good benchmark for the dehumidification levels that could be achieved by a seawater brine which generally consist of $CaCl_2$ and $MgCl_2$ as the major salt constituents. A sample of seawater was thereby heated until the solute content reached their solubility limit. The concentrated seawater brine was then admitted into the experimental configuration. Results are compared against the data obtained from the $CaCl_2$-$MgCl_2$ CELD mixture as shown in Fig. 8 below.
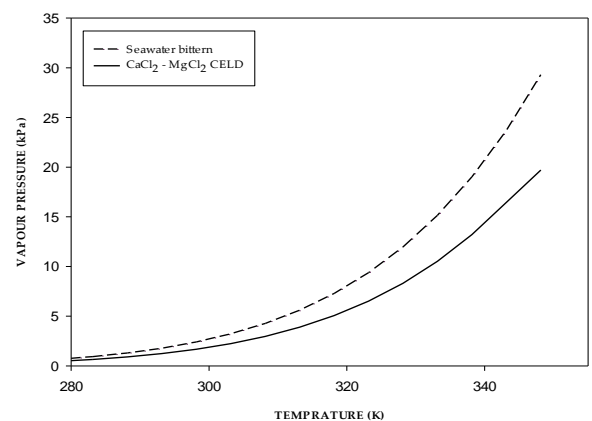

Fig. 8. Comparison of the concentrated seawater brine against the 35 % w/v $CaCl_2$-$MgCl_2$ CELD mixture data.

The concentrated seawater brine solution badly performed relative to the artificial $CaCl_2$-$MgCl_2$ salt solution mixture. The reduction in dehumidification performance was related to the inclusion of additional salts in seawater brine leading to an adverse effect [19]. However, it was nonetheless hypothesized that a salt solution doped with additional $MgCl_2$, $CaCl_2$ or CELD

would potentially improve vapour pressure reductions properties of the liquid desiccant.

4. Conclusions

$MgCl_2$ based desiccant have shown promising results for dehumidification of humid air and provides the possibility of utilizing a source that is ever-abundant due to the desalination industry, in particular.

Vapour pressure has been considered and proven to be an important parameter in the selection process and the differentiation between the different cost-effective liquid desiccants (CELDs). A simple methodology to produce a complete physicochemical database through which new cost-effective liquid desiccants can be obtained has been tested and validated by comparing the experimental data with the already published data from other methods. It is worth mentioning here that, importantly from a sustainable point of view, concentrated seawater brines (waste produced during desalination process) have an excellent performance similar to that of 50% $CaCl_2$ – 50% $MgCl_2$ mixture and may be used as a promising cheap desiccant in the future.

Abbreviations

ERH   equilibrium relative humidity
P_g saturation pressure, kPa
P_v vapour pressure of water, kPa
RH   relative humidity
T   temperature, K

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