Selection of Liquid Desiccants as Working Fluid for Solar Air Conditioning Systems

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Abstract: Desiccants are chemical materials used for air dehumidification, which have applications in air conditioning, drying of agricultural products and in the industry such as pharmaceutical processes. Their effectiveness in air dehumidification differs based on their chemical compounds. Lithium chloride is the most effective salt in air drying and is used in liquid desiccant air conditioning systems. Calcium chloride is an alternative salt for air dehumidification but is less effective and less expensive than lithium chloride. As a consequence a 50-50% mixture of the two substances are usually used as a cost effective liquid desiccant (CELD), which has a good affinity in air dehumidification and at the same time can be purchased at a lower cost compared with lithium chloride. In this paper characteristics of desiccant as a function of temperature, humidity and concentration are studied and desired solution for solar air conditioning system are introduced.

Keywords: Desiccant, Solar air conditioning, Characteristics and lithium chloride

چکیده: موارد جاذب رطوبت مواد شیمیایی هستند که به عنوان ماده رطوبت گیر در سامانه های تهویه مطبوع و سرمایشی و غیره کردن تولیدات شکارچی و در بعضی صنایع مانند صنایع دارویی استفاده می شوند. کاراپی این موارد در رطوبت گیری با توجه به ترکیب شیمیایی آنها متغیر است. در رطوبت گیری های موجود نمک لیتیوم کلراید از کارآپی‌ترین موارد است که در سیستم‌های تهویه مطبوع مكانی کاربرد دارد. اکثریت کلراید ماده دیگری است که از این سیستم‌ها مورد استفاده قرار می‌گیرد ولی کارآپی کمتری داشته و ارزان‌تر است. ترکیب ۵۰ درصد از این دو ماده نیز به عنوان ماده جاذب رطوبت مطبوع و ارزان در سیستم‌های تهویه مطبوع مورد استفاده قرار می‌گیرد. در این مقاله مشخصه‌های جاذب رطوبت مختلف بر اساس دمای رطوبت و غلاف‌های ماده مورد بررسی قرار گرفته و مناسب‌ترین محلول برای سیستم‌های تهویه مطبوع و سرمایش معرفی شده است.

واژه‌های کلیدی: ماده جاذب رطوبت، سامانه‌های تهویه مطبوع، مشخصات و نمک لیتیوم کلراید.
1. Introduction

Desiccants can be either solid, like silica gel, zeolites, synthetic zeolites, carbon, activated alumina and synthetic polymer, or liquid, like calcium chloride, lithium chloride, glycol and lithium bromide. Solid desiccants have a greater drying capacity in comparison to the liquid desiccants. Due to this reason, they have wider applications to dehumidify the supply air in various air-conditioning applications than the liquid desiccants. Factor and Grossman [1], however, listed the following advantages for liquid desiccants: ease of manipulation and mobility, low pressure drop of air-flow across the desiccant material, can be used in filtration to remove dust, and finally they require a lower regeneration temperature compared to solid desiccants.

In this paper, properties of different sorbent solutions and their characteristics in terms of temperature, humidity ratio and solution concentration will be discussed.

2. Selection of Desiccant

In order to select a desiccant material, toxicity, corrosively, stability, boiling and melting points, and mutual solubility in water should be considered as criteria [2]. The maximum allowable melting point of the desiccant depends on the possibility of crystallization.

Among the liquid desiccants, lithium bromide solution has been in common use. Other solutions, such as lithium chloride and calcium chloride, have also been used by many researchers. A mixture of lithium chloride and calcium chloride is also reported to be cost-effective and suitable for air dehumidification applications [3].

Most organic desiccants such as ethylene glycol were not considered due to the fact that a proportion of the vapors will always migrate to the air during the dehumidification and regeneration processes. Even traces of these organic vapors could be harmful. Hence, inorganic salts, which are highly soluble in water, were taken as the suitable candidates for air dehumidification. The following are the most important properties of the candidates likely to be suitable as liquid desiccant [4]:

- High solubility in water.
- Very low water vapor pressure in equilibrium with the saturated solution at ambient temperature.
- High vapor pressure at temperatures between 60 °C and 80 °C, so that the salt solution can be regenerated at these temperatures, easily obtained from flat plate solar collectors.
- Low density and viscosity to minimize pressure drop in the dehumidifier and regenerator.
- Low cost, non-poisonous and non-corrosive.
- Does not undergo undesirable phase transition, which may lead to salt crystallization in the columns.

Search for suitable materials showed that zinc chloride may be included with the salts which have been previously studied [4]. These salts are lithium chloride, lithium bromide and calcium chloride. Sulphuric acid and sodium hydroxide, two of the most effective liquid desiccants were eliminated due to their strong smell, high corrosively, safety and health hazards.

3. Evaluation of Materials used as liquid desiccants

To evaluate desiccant solution candidates for use in liquid desiccant dehumidification systems, an understanding of the simultaneous heat and mass transfer process occurring in the absorber is necessary. Changes in
refrigerant absorption rates per unit area of the absorber brought on by a change of sorbent solution can be very significant in terms of system cost and power requirement. Conversely, Wood et al. have shown that the collector / regenerator area can be increased or decreased significantly as a result of a change in sorbent solution, without significantly affecting system cost or power requirements [5]. To evaluate the sorbent solution candidates chosen, an analytical absorber model was utilized by Ameel et al. to estimate the cooling capacity per unit of the absorber area for each candidate at conditions likely to be encountered in the liquid desiccant system [6]. Experimental studies were not considered since; in general, these studies did not consider a wide enough range of solution parameters to be useful.

Of those liquid desiccant candidates possessing the minimum qualifications to be considered, desiccant cost is of primary concern. Salts such as calcium chloride and zinc chloride cost much less than salts which have traditionally been used in absorption systems such as lithium bromide and lithium chloride. Unfortunately, calcium chloride does not possess the necessary solubility characteristics and zinc chloride is considered to be too viscous and corrosive. However, Heath and Minger [7] have shown that by combining salts such as calcium chloride and lithium chloride, improved solubility characteristics can be expected as well as a possible reduction in viscosity, while achieving a considerable cost reduction relative to pure lithium chloride. Also, Easteal et al. indicate that mixtures of lithium chloride and zinc chloride display significant minima in viscosity at a composition corresponding to the double salt dilithium zinc chloride [8]. Ameel et al. further indicated that mixtures of chlorides of zinc, calcium, and lithium might exhibit more of the desirable characteristics for sorbent solutions than the single salts from which they are comprised [6]. In light of the reduced cost of these mixtures, the solutions of dilithium calcium chloride, dilithium zinc chloride and calcium zinc chloride were chosen as sorbent solutions candidates. Also, for the purpose of comparison, the solutions of lithium bromide, lithium chloride and zinc chloride were investigated.

The sorbent solution physical properties required by Grossman in [9] absorber model were: (a) vapor pressure as a function of concentration and temperature, (b) solubility of the solute as a function of temperature, (c) viscosity as a function of concentration and temperature, (d) density as a function of concentration and temperature, (e) specific heat as a function of concentration, (f) thermal conductivity as a function of concentration and temperature, and (h) heat of absorption as a function of concentration.

4. Humidity-temperature characteristics of liquid desiccants

Figure 1 shows a plot of the humidity ratio of air in equilibrium with the saturated solution of the salts at different temperatures and concentrations [4]. The basic relationship between the vapor pressure ($P_v$) and the humidity ratio ($w$) in kg water vapor per kg dry air is as follows:

$$w = \frac{18P_v}{28.9(760 - P_v)}$$  \hspace{1cm} (1)

Where, $P_v$ is the estimated water vapors pressure above the solution in mm Hg.

Lithium iodide seems to be effective in dehumidifying the air at almost all the
operating temperatures. However, its diluted solution is difficult to regenerate at any temperature. The reason for such peculiar behaviour is the formation of hydrated salts at high temperatures, unlike other salts where the hydrated salts form at low temperatures. For this reason lithium iodide was eliminated from the list of possible candidates of liquid desiccants. Figure (1) shows that the potential of the saturated salts in absorbing water vapour is in the order of \( \text{LiBr} > \text{ZnCl}_2 > \text{LiCl} > \text{CaCl}_2 \). However, it is incorrect to reach conclusions regarding the suitability of the different salts from their saturated solution behaviour. Saturated solutions cannot be employed in practical systems, as any disturbance to the system will lead to salt crystallization, which may cause clogging of the packing in the dehumidifier.

Figures (2) – (5) show the humidity ratio of the air above the salts solutions at different temperatures and concentrations. Lithium bromide and zinc chloride, are the most efficient salts in dehumidifying the air but their solutions must be of high concentrations. Lithium and calcium chlorides require much lower concentrations, with calcium chloride being less effective in dehumidifying the air. In humid countries such as those in South East Asia, a relative humidity of 80% at ambient temperature of 30 °C is a typical day weather condition. The humidity ratio at such condition is 0.021 kg/kg. If the relative humidity is to be reduced to 20%, corresponding to a humidity ratio of the order of 0.005 kg/kg, then 76% of the water vapors must be removed. Such air may be evaporative cooled close to 16 °C.

Figures (2) – (5) show that such dehumidification can be achieved by the different salts with different concentrations: lithium bromide (57%), lithium chloride (40%), calcium chloride (50%) and zinc chloride (70%). For comparison, diethylene glycol requires a concentration of 96%, the remaining 4% being water.

It seems that most of the selected salts are effective in dehumidifying the air at low temperature with calcium chloride being the least effective. However, the required concentration of the salts varies between 40%, to 70%. At such concentrations, the salts may be regenerated at a temperature just above 65 °C, with the exception of the calcium chloride, which may be regenerated below that temperature.

The 96% diethylene glycol requires similar regeneration temperature above 65 °C. These values were calculated from Figures 3.2 to 3.5, assuming the same humid air is used in the regeneration. Either the solution or the air is heated in the regeneration process and a flat plate solar collector may be used for this purpose. If hot dry gases are available then low regeneration temperatures may be employed. In addition to the absorption and regeneration efficiencies of the different salts, other properties such as, density, viscosity, corrosion and cost should be considered during the selection of the salt for air dehumidification. Table 1 shows that the density of the different salt solutions are of the order \( \text{ZnCl}_2 > \text{LiBr} > \text{CaCl}_2 > \text{LiCl} \) within the operating range of concentration and temperature discussed in the previous section [4]. The viscosity of the salts, at these operating conditions follows similar trends as shown in Table (2).

The higher the density and viscosity of the solution, the higher the pumping power required. According to this criterion, lithium and calcium chlorides should be the choice. If the choice has to be made between \( \text{ZnCl}_2 \) and \( \text{LiBr} \), then \( \text{ZnCl}_2 \) should be selected.
owing to its lower cost. In addition, ZnCl$_2$ is the only salt that does not form hydrated crystals and this eliminates the possibility of complete solidification of the desiccant solution.

Most non-metal surfaces have good resistance to the four salts studied. Many metals have fair resistance to corrosion by the solutions of the different salts, with the exception of ZnCl$_2$, which requires the use of metal alloys [10].

5. Properties of liquid desiccant mixtures

Liquid desiccants can be mixed to get a salt solution, which has optimum properties compared with the individual desiccant solution. As an example, lithium chloride is the most stable liquid desiccant and has a large dehydration concentration (30% to 45%), but its cost is relatively high ($24.00-48.00 per kg.). Calcium chloride is the cheapest ($6 per kg) and most readily available desiccant, but it has the disadvantage of being unstable depending on the air inlet conditions and the concentration of the desiccant in the solution. To stabilize calcium chloride and to decrease the high cost of lithium chloride, the two can be mixed in different weight combinations. Properties of different combinations of this mixture such as density, viscosity, vapour pressure which are necessary for analysis of heat and mass transfer in desiccant-air contact systems have been measured [11].

5.1. Vapour pressure of the mixture

As already described, for dehumidification to occur the vapor pressure of the desiccant must be lower than the vapor pressure of the air. In other words, the driving force for dehumidification is the vapor pressure difference between the desiccant and the air. Hence, its vapor pressure can measure the performance of a desiccant. The lower the vapor pressure, the better a desiccant performs. The poor performance of calcium chloride is due to its high vapor pressure compared to lithium chloride. Since the resulting new liquid desiccant mixture will have a lower vapour pressure compared to calcium chloride, extraction of moisture from the air will be improved. From the foregoing discussion, it is clear that vapor pressure is a unique identifying property of a desiccant. The vapor pressure of a solution is the pressure of the vapor that is in equilibrium with the solution at a given temperature. Vapor pressures of the mixture of lithium chloride and calcium chloride have been experimentally measured [11]. The purity of the two salts that they used to form the mixture was 99.3% and 90%, respectively. Several different combinations of the lithium and calcium chloride solutions’ vapor pressure were studied and the results are shown in Figures 3.6 to 3.8. The results displayed in these figures provide the basis for selecting the LiCl / CaCl$_2$ mixture ratio to be used in the dehumidifier of the liquid desiccant cooling system. Figure 3.6 presents the vapour pressure in a 20% concentration solution as a function of the LiCl / CaCl$_2$ mixture ratio (by weight) and temperature. The LiCl / CaCl$_2$ mixture ratio varies from 0% (100% CaCl$_2$) to 100% (100% LiCl). The addition of LiCl to CaCl$_2$ clearly reduces the vapour pressure in a nonlinear fashion at all temperatures.

Figure (7) shows the vapors pressure as a function of the LiCl / CaCl$_2$ mixture ratio at 26.6 °C and 32.2 °C. The rate of the vapors pressure decrease is greater over the first 50% of mixture ratio than the last 50%. In fact, the reduction in the vapors pressure over the last 50% of the LiCl / CaCl$_2$ mixture ratio, is only about 40% of that over the first 50% of the mixture ratio. Since the cost of LiCl is considerably greater than the cost of CaCl$_2$, one should hold the mixture
ratio as low as possible while maintaining the dehumidifier performance. On the basis of cost and performance, a 50% LiCl / CaCl₂ mixture ratio was selected.

A comparison has been made between the vapor pressures for LiCl and CaCl₂ obtained by [11] and those reported by [12, 13]. Table 3 compares the partial pressure of water vapor over lithium chloride solution measured at 20% concentration. It is interesting to note that the deviation varies from 2 to 20% with the [11] result taken as the base. The deviation may be mainly due to the purity of the desiccant. Further, it can be seen that the deviation is large at low temperatures and that as the temperature increases the deviation decreases. The same conclusion is drawn when the partial pressure of the water vapor of calcium chloride is compared, which is shown in Table 4.

6. Properties of the CELD solution

The physical properties of the Cost Effective Liquid Desiccant (CELD), which is a 50% mixture of LiCl and CaCl₂ such as vapors pressure, density, viscosity and solubility as measured experimentally in [11] are presented in Figs. (8)-(12). Since the accuracy of the vapor pressure measurement of a liquid desiccant at low temperatures with high concentration is very poor, the vapors pressures of 20 mm of Hg and the lower values was estimated using an experimental approximation. Also, the same approximation has been done for the values of vapors pressures corresponding to temperatures higher than 60 °C. As shown in Fig. (8), the performance of the CELD improves as the concentration increases. However, the vapors pressures are comparatively close at temperatures between 20 °C and 35 °C.

The density of the CELD solution against various temperatures and for different concentrations is plotted in Fig. (9). From the observed data, all of the density curves follow the same trend and the change in density is linear for different concentrations. One can conclude that the consistency of the experimental results is evident by the identical nature of the curves in Fig. (9).

The results of the viscosity measurement at 40% concentration as shown in Figure 3.10 indicate that the solution favors the calcium chloride solution. It is interesting to note that low viscosity is one of the requirements for an effective liquid desiccant. Hence, as far as viscosity is concerned, CELD has a better range of viscosity compared to lithium chloride. The viscosity of the CELD solution at various temperatures and concentrations is plotted in Fig. (11). As shown in this figure, at the higher concentrations, a considerable amount of change in viscosity was observed. For low concentration of CELD, viscosity decreases, this is expected.

Both calcium chloride and lithium chloride are highly soluble in water at ordinary temperatures. However, solid phase separation will occur at certain concentration and temperature combinations. One should expect the same situations from the CELD, and determination of solubility for the identification of this new solution is essential.

The solubility of a test solution as indicated in Fig. (12), tends to follow that of calcium chloride for temperatures less than 23 °C. Conversely, above this temperature, observed data points tend to follow the lithium chloride solution. For solution concentrations higher than 46 % wt, the required solubility temperature changes widely. As an example, for a 48 % wt, solution of calcium chloride, lithium
chloride and CELD, the solubility temperatures are 26 °C, 38 °C and 53 °C, respectively. However, this temperature change for solubility at concentrations less than 46 wt % is not considerable since all three solutions behave similarly. As shown in Fig. (12), saturating phase for calcium chloride occurs at approximately 23 °C, whereas for lithium chloride, saturating phase occurs at 20 °C. Note that a new saturation phase for CELD occurs at 26 °C, almost in the same region as the other two liquid desiccants. As shown in the figure, smoothness of the CELD solution curve supports the reliability of the data points. From the solubility results, one can conclude that the solubility of CELD is sufficiently high in water at ordinary temperatures.

7. Corrosion and Wetting Performance of the Desiccants

As was already described, desiccants can be corrosive when subjected to metal surfaces such as ducts or pipes. This can be avoided either by selecting a less corrosive desiccant such as calcium chloride solution or substituting nonmetals such as polyester based materials for the metals. Another alternative is the use of corrosion inhibitors, such as lithium chromate in the desiccant solution [14].

The wetting characteristic of the absorber plates is another issue, which should be considered when selecting the desiccant and plate material. In order to increase the dehumidification efficiency of a liquid desiccant system good wetting properties of the desiccant on the absorber plates has to be maintained. Selecting the proper material for the plates can do this. Metals wet very well, but are not recommended, due to highly corrosive action of the desiccant. In addition to plate material, selection of the proper distribution mechanism (such as spray, etc.) may have a significant effect on the wetting.

According to experiments carried out by the Gas Research Institute on corrosion and wetting performance of desiccants, especially lithium chloride, ‘Flocked’ polyester films show the best behavior among the plastic materials tested [14]. Several other types of plastics have been proposed that are polyester based with flocking or similar surface treatment.

8. Hazardous effects of desiccants

Many desiccants can be harmful to human health and should be prevented from contact with the body and skin. Different methods were described in order to prevent the desiccant droplets from entering the conditioned space. According to the ChemWatch Material Safety Data Sheet (2002), calcium-chloride is less hazardous than lithium-chloride and it is also less corrosive to the metals [15]. Consequently, if a mixture of the two salts has to be used as the desiccant, it is desirable to use higher ratios of calcium chloride in the mixture to reduce the hazardous and corrosion problems. Inorganic absorbents such as sulphuric acid, etc., have a hazardous nature and are not to be used. Due to the above reasons calcium chloride solution, which is less hazardous and less expensive has been selected as the liquid desiccant for experimental work.

9. Sanitizing effects of desiccant-based cooling

Airborne microorganisms (bio-aerosols) are responsible for numerous disease outbreaks [16]. The relationship between bio-aerosols and airborne disease transmission in the medical community has been well established [17]. Outbreaks of tuberculosis, chicken pox, measles and small pox have confirmed the importance of airborne disease transmission [17]. However, the impact of bio-aerosols on indoor air quality [19] has only recently
been examined. Bacterial and fungal infections in health care facilities and research laboratories are often disseminated through HVAC systems [20]. Similarly, indoor air quality (IAQ) studies are finding that bio-aerosols are a primary link to building-related illness (BRI), infections, toxic syndromes and hyper-sensitivity diseases [21].

Since the early 1980s, illness and complaints associated with indoor air quality have been steadily climbing. Indoor air quality investigations conducted by the National Institute for Occupational Safety and Health [22] during the 1980’s, found bio-contaminants to be responsible in 5% of problem buildings. Other investigators have found microorganisms to be the primary cause in as many as 35-50% of IAQ cases [23]. The increase in both communicable disease rates and BRI is often attributed to insufficient ventilation or re-circulated air. Many studies identify inadequate fresh air as a primary cause of IAQ problems [23].

However, increasing the amount of fresh air (without pre-conditioning) can also increase the level of humidity. Excess moisture (above 60% relative humidity) provides conditions, which allow fungi to proliferate. Since bio-aerosols are associated with moisture, maintaining relative humidity below 60% will aid in their control [25]. In addition to controlling bio-contaminants, maintaining the health of building occupants largely depends upon maintaining the proper range of temperature, humidity and ventilation (comfort criteria). Since comfort criteria are controlled by HVAC systems, an HVAC system, which combines these principles, may be useful in achieving this goal.

As was described in the previous chapters in a desiccant-based air conditioning (DBAC) system a desiccant material, which can be either liquid or solid, is used to dehumidify air. Hines et al. [26] noted that desiccant systems can enhance the quality of indoor air and reduce the level of microorganisms.

Four desiccant-based air conditioning systems using solid desiccant wheels were evaluated by Phillips and Wagner [27] to determine their effectiveness in reducing bio-aerosols. Field studies were conducted on three of the DBAC units to observe their performance under normal operational conditions. The three DBAC units were installed in health care facilities, where bio-aerosols (particularly bacteria and fungi) can be a constant problem. Two of the units were located in patient areas in local hospitals (sites 1 & 2) and, one unit was located in a commons room in a nursing home (site 3).

For the laboratory study, one DBAC unit was installed in a climate controlled isolation chamber in a university microbiology laboratory to evaluate the effects of the DBAC system on the seven selected microorganisms. In addition to testing the system on specific microorganisms, the laboratory study also isolated and examined the effect of the desiccant wheel. The results of the field and laboratory studies are presented in Figs. (13) and (14), respectively. As Fig. (13) shows, all three of the field study sites displayed reductions in both bacteria and fungi across the DBAC unit. An overall reduction was also observed in six of the seven organisms tested across the DBAC unit as shown in Fig. (14).

10. Conclusion

In selecting a desiccant absorbent for liquid desiccant dehumidification cooling system different characteristics such as toxicity, corrosion, stability etc., should be
considered as criteria. Of those liquid desiccant candidates possessing the minimum qualifications, desiccant cost is also of primary concern. However, it has been shown that by combining salts, improved characteristics can be expected while achieving considerable cost reduction relative to the pure salts.

Among the desiccants, lithium chloride and calcium chloride are in common use. Lithium chloride is the most effective in dehumidifying the air but the most expensive. Calcium chloride, which is the cheapest has less effectiveness in the air dehumidification and is less hazardous. A combination of these two salts can be used in order to increase the effectiveness of calcium chloride and decrease the high cost of lithium chloride. A 50% combination, known as Cost Effective Liquid Desiccant (CELD), has been proposed by Ertas et al. (1992) to be the best combination. However, in this study calcium chloride, due to being less expensive and less hazardous, has been selected as the desiccant.

The health hazard in liquid desiccant systems, despite the fact that they have sanitizing effects on airborne microorganisms, is an important issue and has to be taken into consideration. In the proposed system, a baffle can be incorporated in the final stage to capture any desiccant droplets, which may be carried over by the air. Alternatively, a demister could be used in the dehumidifier to capture the liquid desiccant droplets. The introduction of a direct evaporative cooling pad as a cooling stage will also ensure that traces of desiccant material are not carried into the conditioned space. It is notable that lithium chloride can be regenerated by temperatures as low as 40 °C. Therefore low cost flat plate collectors could be used which can produce high temperature hot water in summer.

11. References


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Fig. (1): Humidity ratio of air above different saturated solutions [4].

Fig. (2): Humidity ratio of air above unsaturated solutions of LiBr [4].

Fig. (3): Humidity ratio of air above unsaturated solutions of LiCl [4].

Fig. (4): Humidity ratio of air above unsaturated solutions of CaCl₂ [4].
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Fig. (5): Humidity ratio of air above unsaturated solutions of ZnCl₂ [4]

Fig. (6): Vapour pressure of various mixture ratios at 20% concentration [11].

Fig. (7): Vapour pressure of various mixture ratios at 20% concentration [11].

Fig. (8): Vapour pressure of CELD solutions for different weight concentrations [11].

Fig. (9): Density of CELD solution [11].

Fig. (10): Viscosity comparison at 40% concentration [11].

Fig. (11): Viscosity of CELD solution at different concentrations [11].
Fig.(12): Solubility comparison of various desiccants [11].

Fig.(13): Bacteria and fungi reduction in the field DBAC units [27].

Fig.(14): Reductions of the seven organisms tested in the laboratory [27].

Table (1): Density of the salt solutions at the operating conditions [4].

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Table (2): Viscosity of the salt solutions at the operating conditions [4].

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Table (3): Vapor pressure of LiCl at 20% concentration.

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Table (4): Vapor pressure of CaCl₂ at 20% concentration.

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<th>Temperature °C</th>
<th>Vapour pressure (mm Hg)</th>
<th>Vapour pressure (mm Hg)</th>
<th>Deviation (%)</th>
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