

A PRELIMINARY EVALUATION OF ALTERNATIVE LIQUID DESICCANTS
FOR A HYBRID DESICCANT AIR CONDITIONER

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ABSTRACT

This paper presents the results of a preliminary investigation at The University of Texas at Austin of alternative liquid desiccants for use in a hybrid desiccant air-conditioning system in which a desiccant is circulated between the evaporator and the condenser of a vapor-compression air conditioner. The liquid desiccants studied were lithium chloride, lithium bromide, calcium chloride, and triethylene glycol. Each candidate desiccant was subjected to a screening process which weighed the merits of the desiccant in terms of selected characteristics. The best liquid desiccant for the anticipated application was found to be calcium chloride.

INTRODUCTION

Desiccant dehumidification air-conditioning systems have excellent potential for cost-effective application in commercial buildings located in hot, humid climates. Hybrid liquid desiccant/vapor-compression air-conditioning systems, in particular, are promising because they take advantage of the high efficiency for heat transfer inherent in vapor-compression systems and the high mass transfer potential of the liquid desiccants. However, to be cost effective, hybrid systems must provide operational savings over competing vapor-compression air-conditioning systems and/or be less costly to manufacture. In the hybrid air-conditioning system shown in Figure 1, a desiccant is circulated between the evaporator and condenser of a vapor-compression air conditioner providing both operational and first-cost savings.

A preliminary evaluation of the thermodynamic potential with a slight variation of the system shown in Figure 1 was conducted by Howell and Peterson¹. Considerable potential was shown for saving energy and reducing peak electric demand over conventional vapor-compression systems when providing the same outlet air conditions.

Continuing analytical work at The University of Texas has shown potential first-cost savings resulting in a 34% reduction in the exchange area for both the evaporator and condenser and a 25% reduction in the required compressor capacity. Additionally, electric power drawn by the compressor is expected to drop by 25%, resulting in savings on electric utility bills. These savings are possible without sacrificing cooling efficiency or thermal comfort.

Given the promising economics, a preliminary investigation of alternative liquid desiccants for use in the hybrid desiccant system shown in Figure

1 was initiated. This paper presents the results of this investigation to identify the most promising liquid desiccant from among the following candidates: lithium chloride (LiCl), lithium bromide (LiBr), calcium chloride (CaCl₂), and triethylene glycol (TEG).

APPROACH

Each candidate desiccant was subjected to a screening process that weighs the merits of the desiccant in terms of the characteristics shown in Table 1. A maximum weighting, or weighting factor, was assigned to each characteristic depending upon the importance of the characteristic to the researchers. An actual value, or relative weight, is assigned depending upon an objective figure of merit for the characteristics being considered, e.g., LD50 for safety. In the final analysis, the product of weighting factors and relative weight are summed for each characteristic and the candidate with the highest total is selected as the best desiccant for the anticipated application.

A literature search was conducted to obtain relevant data so that figures of merit could be developed for the screening of candidate desiccant solutions. The figures of merit used are shown in Table 1. The sources of the data are referenced in the following discussion.

Table 1 Weighting Factors and Figures of Merit

Characteristic	Weighting Factors	Figure of Merit
Safety	1.0	Lethal dose (LD50)
Corrosion	0.8	Corrosion rate
Mass transfer potential	0.8	Equilibrium vapor pressure
Heat of mixing	0.6	Energy/lb water absorbed
Cost of desiccant	0.5	\$/100 lbs solution
Heat transfer potential	0.5	Thermal conductivity
Parasitic power losses	0.3	Viscosity

DISCUSSION

SAFETY

Since the liquid desiccants will be in direct contact with conditioned air, it is important to investigate any possible effects of ingestion, inhalation, or skin contact. One source of

information is the Material Safety Data Sheet (MSDS) available for most chemicals produced in the United States, whose form and content are designated by the Occupational Safety and Health Administration. The MSDS is provided by the supplier of each chemical and contains information such as physical data, fire and explosion hazard data, health hazard data, reactivity data, spill or leak procedures, and special handling or protection information. Review of the MSDS for TEG, LiCl, CaCl₂, and LiBr indicates that none of these chemicals poses a health hazard when used in the system to dehumidify air. There are adverse effects such as nausea due to ingestion of these chemicals, but the desiccants are considered toxic only in large amounts.

The candidate desiccants have toxicity ratings from moderate (LiCl) to low (CaCl₂) to relatively nontoxic (TEG). One measure of toxicity is the LD50 dose, which is the lethal dose that will result in fatality 50% of the time. Lithium chloride has an LD50 of approximately 1.23 oz (35 g) of the pure chemical for an average person when taken orally². Lithium bromide has an LD50 for mice of 1.68g/kg, which would correspond to approximately 4.03 oz (114 g) for an average person³. The LD50 for calcium chloride is approximately the same as that for table salt, 5.30 oz (150 g)⁴. The LD50 for TEG is reported to be 52.7 oz (1,496 g) for an average person⁵. The next most likely method of ingestion of one of these chemicals, after oral ingestion, is the inhalation of a mist containing one of these chemicals.

The possibility of inhalation of a mist containing one of these chemicals could exist due to the direct exposure of a liquid desiccant to the air stream. No evidence of adverse effects exists for inhalation of TEG vapors at normal temperatures. Overexposure to TEG vapors generated at high temperatures may result in respiratory tract irritation and in the inhalation of harmful amounts of the material⁶. The three salt solutions

have similar behavior in terms of inhalation concerns. Air blown over solutions of lithium chloride, lithium bromide, and calcium chloride contain no hazardous constituents; however, salt solutions may irritate eyes or lungs if a mist is generated^{2,3,7}. Since lithium compounds do not accumulate in the body, only chronic overexposure to lithium would produce adverse side effects⁸. Effective means of removing entrained mist should be included in any system using one of these desiccants.

Skin contact with saline solutions or TEG could cause minimal irritation. The possibility of solutions drying out and leaving residue on the equipment and distribution ductwork is a small problem because these materials readily absorb water, thereby maintaining the desiccant in solution.

Table 2 Figures of Merit for Safety

Desiccant	LD50 (oz)	Relative Weight
LiCl	1.23	7
LiBr	4.03	8
CaCl ₂	5.30	9
TEG	52.7	10

The saline desiccants are described as odorless, while triethylene glycol is described as having a mild odor.

CORROSION

Corrosive liquid desiccants should be avoided for long life and reliable operation of the hybrid system. The saline solutions represent one family of corrosion problems due to the presence of the electrolytic halide ions, and TEG represents another.

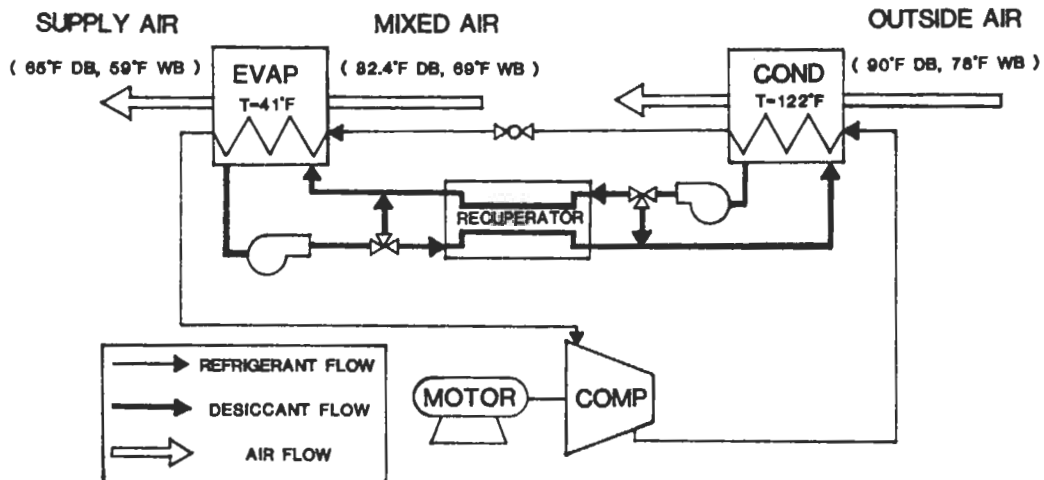


Figure 1 The Proposed Hybrid Vapor Compression/Liquid Desiccant Air Conditioning System

The open design configuration of the absorber unit allows atmospheric oxygen and carbon dioxide to be dissolved into the desiccant solution as it flows over the absorber. Dissolved oxygen and carbon dioxide increase the corrosion rates of most metals⁹. One method of corrosion control is the use of inhibitors in the solution. Uninhibited solutions of calcium chloride have surface corrosion rates in the 2 to 20 mils/year (mpy) range for aluminum, steel, and copper¹⁰. Stainless steels are usually considered poor choices for chloride environments⁹ and are seen to have corrosion rates greater than 20 mpy and in some cases greater than 50 mpy¹⁰. A satisfactory corrosion rate would be less than 2 mpy. A manufacturer of lithium chloride dehumidifiers reports that the use of hot-dipped galvanized steel components has resulted in 25 years of useful service in these dehumidifiers¹¹. A supplier of lithium chemicals recommends the use of lithium chromate and lithium molybdate as inhibitors for copper/nickel alloys used in some dehumidifiers that apply lithium chloride solution as a desiccant. Lithium chromate is also an effective inhibitor for LiBr solutions, as seen in one study where the corrosion rate of plain carbon steel in an inhibited 54% LiBr solution was 0.55 mpy, approximately one-tenth of the uninhibited value of 5.7 mpy¹².

Corrosion rates in TEG solutions are low for most metals, including aluminum, copper, and steel. Reported rates of corrosion are less than 2 mpy for these materials¹³. Copper used in TEG air-conditioning systems has reported rates of corrosion from 0.1 to 1 mpy at 320°F (160°C). Aerated solutions of TEG at room temperature are reported to have insignificant corrosion rates for copper¹⁴.

Table 3 Figures of Merit for Corrosion

Desiccant	Corrosion Rate (mpy)	Relative Weight
LiCl	Insignificant for inhibited solutions	10
LiBr	0.55	10
CaCl ₂	2 to 20 for uninhibited solutions	9
TEG	Insignificant	10

MASS TRANSFER POTENTIAL

The property that most clearly identifies the potential of a desiccant solution to remove water vapor from a process air stream is the equilibrium vapor pressure of water in solution. When the vapor pressure of a solution is less than that of the air, water vapor will be sorbed into solution. As more water vapor is sorbed, the solution is diluted and the vapor pressure increases until the water vapor being sorbed from the air equals the water vapor desorbed from the desiccant solution, i.e., until equilibrium and an equilibrium vapor pressure is achieved. Conversely, when the vapor pressure of the solution is greater than that of the air, water is desorbed until equilibrium and an equilibrium vapor pressure with the process air is

achieved. Thus a potential for mass transfer exists to dehumidify air or to regenerate a desiccant whenever a nonequilibrium condition is created.

A desirable candidate liquid desiccant solution is one that has sufficiently low equilibrium vapor pressure when sorbing and sufficiently high equilibrium vapor pressure when being regenerated. Since the equilibrium vapor pressure of a desiccant solution is a function of concentration and temperature, either of these can be varied to improve the potential for mass transfer. However, for the hybrid system being studied at The University of Texas, the rated sorbing and desorbing temperatures are specified as 41° F (5° C) and 122° F (50° C), respectively. Consequently, only solution concentration can be varied independently to promote mass transfer during operation at design conditions.

The limiting concentration for any application of salt solutions is the crystallization point. This maximum allowable concentration decreases with temperature and, for the system under study, the temperature of interest is 41° F. A 5% concentration safety margin is desired to ensure that crystallization will not occur.

The maximum concentration for the desiccant solutions, along with the concentration used for all property evaluations in this study, is shown in Table 4. These concentrations were specified in the design to obtain an equilibrium vapor pressure of 0.13 inches (3 mm) of mercury, i.e., the rated sorbing equilibrium vapor pressure of the hybrid system studied at The University of Texas at Austin. These concentrations provide the requisite 5% safety margin.

Table 4 Maximum Concentration for Desiccant Solutions at 41° F (5° C)

Desiccant	Crystallization Point (weight %)	Maximum Concentration (weight %)
LiCl	42 ¹⁵	25
LiBr	57 ¹⁶	40
CaCl ₂	39 ¹⁷	34
TEG	N/A	85

Note that TEG has no such crystallization point, although it does glass over at temperatures and concentrations outside those of the expected system operating envelope. Assuming the solutions are regenerated to the maximum concentration, the equilibrium vapor pressures associated with the absorber and regenerator temperatures will indicate the potential for mass transfer. These equilibrium vapor pressures are shown in Tables 5 and 6.

HEAT OF MIXING

The heat of mixing (differential heat of solution) is the amount of heat liberated by the absorption of water into a solution of desiccant at a fixed concentration. The differential heat of solution of water can be calculated from integral heat of solution data. The addition of 1 lb of water to a very large quantity of desiccant solution will cause no detectable change in

solution concentration. The heat that is released when 1 lb of water is absorbed into a solution at the maximum concentration specified in Table 4 is shown in Table 7. In addition to the latent heat of vaporization, this heat must be removed by the cooling system. Therefore, a relatively low heat of mixing is desirable.

Table 5 Figures of Merit for Mass Transfer Potential at Absorber (41° F)

Desiccant	Equilibrium Vapor Pressure (in. of Hg)	Relative Weight
LiCl	0.13 ¹⁵	10
LiBr	0.13 ¹⁸	10
CaCl ₂	0.13 ¹⁷	10
TEG	0.13 ⁵	10

Table 6 Figures of Merit for Mass Transfer Potential at Regenerator (122° F)

Desiccant	Equilibrium Vapor Pressure (in. of Hg)	Relative Weight
LiCl	2.01 ¹⁵	10
LiBr	1.97 ¹⁸	10
CaCl ₂	1.97 ¹⁷	10
TEG	1.97 ⁵	10

Table 7 Figures of Merit for Heat of Mixing

Desiccant	Heat of Mixing (Btu/lb water)	Relative Weight
LiCl	31 ¹⁵	7
LiBr	17 ¹⁶	9
CaCl ₂	25 ¹⁹	8
TEG	12 ²⁰	10

COST OF DESICCANT

Since the four candidate liquid desiccants have the same mass transfer potential when regenerated to their maximum concentration, the resulting solutions will absorb the same amount of water in the absorber. Therefore, the cost of desiccant to create 100 lbs of solution at maximum concentration, considering the figure of merit for cost, is shown in Table 8 for the four candidates. Prices are telephone quotes taken during the spring of 1988.

HEAT TRANSFER POTENTIAL

The thermal conductivity of the solutions represents an important factor in limiting the performance of the hybrid desiccant air conditioner because mass transfer is accompanied by simultaneous heat transfer. The thermal conductivity of the four candidate solutions at 41° F is given in Table 9.

Table 8 Figures of Merit for Cost of Desiccant

Desiccant	Cost (\$/ 100 lbs solution)	Relative Weight
LiCl	77	7
LiBr	174	5
CaCl ₂	15	10
TEG	38	9

Table 9 Figures of Merit for Thermal Conductivity

Desiccant	Thermal Conductivity (Btu/h-ft-°F)	Relative Weight
LiCl	0.301 ¹⁵	10
LiBr	0.260 ¹⁶	9
CaCl ₂	0.306 ¹⁸	10
TEG	0.162 ²¹	5

PARASITIC POWER LOSSES

The viscosity of the solutions at 41° F and maximum concentration represents the maximum viscosity within the system. This viscosity is important in determining the pumping power required for circulation of the desiccant. Assuming all other factors are equal, the pumping power required is proportional to the viscosity of the solution.

Table 10 Figures of Merit for Viscosity

Desiccant	Viscosity (centipoise)	Relative Weight
LiCl	4 ¹⁵	10
LiBr	3 ¹⁶	10
CaCl ₂	8 ¹⁷	9
TEG	65 ⁵	5

CONCLUSIONS

The screening process is concluded by summing the weights of the characteristics for each candidate as shown in Table 11. The weighting is the product of the relative weight and the weighting factor given in Table 1.

Table 11 Weighting Summary

Characteristic (Max Weight)	LiCl	LiBr	CaCl ₂	TEG
Safety(1.0)	7.0	8.0	9.0	10.0
Corrosion(0.8)	8.0	8.0	7.2	8.0
Mass transfer potential at absorber(0.8)	8.0	8.0	8.0	8.0
Mass transfer potential at regenerator(0.8)	8.0	8.0	8.0	8.0
Heat of mixing(0.6)	4.2	5.4	4.8	6.0
Cost(0.5)	3.5	2.5	5.0	4.5
Heat transfer potential (0.5)	5.0	4.5	5.0	2.5
Parasitic power losses (0.3)	3.0	3.0	2.7	1.5
Total	46.7	47.4	49.7	48.5

According to the weighting system developed in this paper, the best liquid desiccant for the anticipated application is CaCl_2 . The high heat transfer potential and low cost are the primary advantages of using calcium chloride. Further research plans include construction of an experimental absorber/regenerator apparatus and improved computer modeling of the hybrid liquid desiccant/vapor-compression system.

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