Absorption of Water Vapor into New Working Fluids for Absorption Refrigeration Systems

Antonio De Lucas, Marina Donate, and Juan F. Rodrı́guez

Department of Chemical Engineering, University of Castilla, La Mancha, Avda. de Camilo José Cela s/n, 13004 Ciudad Real, Spain

The mass transfer characteristics of water vapor absorption into mixtures of lithium bromide and organic salts of sodium and potassium (formate, acetate, and lactate) were experimentally investigated, in order to select the mixture that presents better properties for its use in absorption refrigeration cycles. The main objective is to overcome the limitations of lithium bromide and improve the characteristics and efficiency of the refrigeration cycle. Taking into account the aspect of operating range and mass transfer characteristics, the LiBr + CHO₂Na (sodium formate) + water (LiBr/CHO₂Na = 2 by mass) could be a promising working fluid as an alternative to the LiBr + water solution.

Introduction

Technology developments have made absorption refrigeration an economic and effective alternative to the vapor compression cooling cycle. The increase in electricity cost and environmental problems has made this heat-operated cycle more attractive for both residential and industrial applications. Absorption chillers are widely used in the air-conditioning industry, in part because they can be activated by hot water, steam, and direct-fired natural gas, among others, instead of electricity.1–3 A conventional absorption chiller consisting of a generator, absorber, condenser, and evaporator requires an additional water cooling tower in order to remove heat and maintain desirable temperatures in absorber and condenser units.4

The overall performance of an absorption heat pump is greatly affected by the characteristics of heat and mass transfer in the absorber where the refrigerant vapor is absorbed into the absorbent.5,6 The refrigeration capacity of an absorption refrigeration engine is limited by the absorption ability of the absorbent solution. In other words, for a given amount of absorbent solution in the machine, its duty is directly determined by the amount of refrigerant that it can absorb. One of the most important considerations for enhancing the performance of an absorption chiller using water as a refrigerant is to improve the performance of the absorber.

Theoretically the mass transfer driving potential during absorption is the difference between the vapor pressure of the refrigerant (water vapor) and the vapor pressure of the absorbent at the concentration and temperature where absorption takes places. Nevertheless, the mass transfer ability of the absorbent solution greatly depends on the physicochemical properties of the absorbent solution. Addition of substances with tensioactive properties such as heavy linear alcohols5 and a variety of mechanical and physicochemical methods have been adopted for the improvement of absorber performance. Another possible mechanical way is to increase the waviness of the vertically falling film absorber. Increases between 50 and 200% in terms of the mass transfer coefficient by the wavy motion were reported experimentally for the LiBr + water solutions.7–10

Water is one of the most acceptable natural refrigerants, because of its safety and cost. Lithium bromide was chosen as absorbent because it meets the following desired solution characteristics for the absorption refrigeration systems: stability in aqueous solution and low vapor pressure at absorber conditions. The drawbacks of many working fluids, such as lithium bromide, are that they crystallize at high concentrations, are corrosive to metals, and are very expensive.

One of the more serious limitations of lithium bromide solutions as absorbent solutions for refrigeration engines is the high temperature necessary in the generator to reach the boiling point. The conventional operation conditions in the generator vessel of these machines used to be 373.15 K at 10 kPa for a LiBr concentration of 60%.11 At this pressure level the boiling point for pure water is about 320 K. This high ebullioscopy increase is due to the elevated concentration of the lithium bromide solution.12 A big challenge to enlarge the field of application of this kind of machine is to reduce the temperature of the hot fluid used to produce boiling of the dilute solution in the generator section. This allows streams to be applied with lower temperature as condensates or hot water from solar energy collectors.

Various new working fluids have been developed to improve the performance characteristics of the conventional lithium bromide + water system.13–15 Between them, potassium formate is cited in literature because of its physical properties and absorption—desorption rates, which would make it suitable for its use in an absorption cycle. Potassium formate shows a crystallization temperature, density, and viscosity lower than that of lithium bromide, smaller vapor pressures, alkaline pH, and less toxicity, and is biodegradable.14 Potassium formate has a good compatibility with conventional absorption fluid additives and may be used in conjunction with other known absorbents such as lithium bromide to provide mixed salt brine formulations to enhance their performance by reducing their crystallization temperature and to protect labile components from oxidative degradation.14

In previous papers, mixtures of lithium bromide and organic salts of sodium and potassium (formate, acetate, and lactate) have been thermodynamically evaluated as alternative absorbents for absorption refrigeration machines. In order to select the mixture that presents better properties for its use in absorption refrigeration cycles, a thermodynamic analysis was performed on the basis of similar absorption behaviors to that of LiBr. These mixtures show optimal properties: low vapor pressures due to lithium bromide, and lower crystallization temperature and latent heat of absorption due to the organic salt, that could provide better operation coefficients and economic advantages. Among those properties tested, the lower temperature required in the generator is the most significant, which would permit the use of waste streams, with a lower calorific content.16–19

* To whom correspondence should be addressed. E-mail: juanfran@inqu-cr.uclm.es.
The main advantage of these mixtures is the low heating requirements in the generator section. A stream with a $\Delta T \approx 10$ K over 334.15 K to reach the boiling point of the diluted absorbent mixture is adequate. This allows the use of condensate water, or any other residual stream of the industrial process and not necessarily overheated water or steam, even under 383.15 K, to evaporate the absorbent mixture. Nevertheless, if the absorption capacity of these mixtures is not at the same level as the traditional LiBr, the aforementioned advantage would be limited by the decrease of refrigeration capacity that would allow its use in the same refrigeration engine.

The objective of this work focused on providing experimental information that was observed upon mass transfer in the mixtures of lithium bromide and organic salts of sodium and potassium and comparing it with that of lithium bromide. The working fluids treated in this work are LiBr + water, LiBr + CHO$_2$Na (sodium formate) + water (LiBr/CHO$_2$Na = 2 by mass), LiBr + CHO$_2$K (potassium formate) + water (LiBr/CHO$_2$K = 2 by mass), LiBr + CH$_3$CO$_2$K (potassium acetate) + water (LiBr/CH$_3$CO$_2$K = 2 by mass), and LiBr + CH$_3$CH(OH)CO$_2$Na (sodium lactate) + water (LiBr/CH$_3$CH(OH)CO$_2$Na = 2 by mass).

Experimental Section

The schematic diagram of the experimental absorption device is presented in Figure 1a, and the detail of the column with the nomenclature of the streams is shown in Figure 1b. The major compartments of the system consist of an absorber, an evaporator, a cooling water system, a circulation system, a vacuum-generating part, a measuring device, and a sampling device.
The main part of the absorber was constructed using two concentric glass tubes. Inside the external tube, the cooling water was circulated to remove the heat of absorption in a countercurrent manner during vapor absorption on the inner wetted tube surface. The strong solution (before absorption) was fed to the top of the absorber using the solution pump. Inside the inner tube, a nonstructural packing of glass raschig rings was used to favor the contact between the strong solution and the vapor refrigerant. The characteristics of the packing material are shown in Table 1. A 0.5 L spherical Pyrex vessel was used as an evaporator device. The heat of vaporization was provided by means of an electrical heater. The absorption temperature was maintained at a fixed value using a thermostatic bath. It can provide a flow rate of up to 160 kg/h, which is sufficient to maintain the temperature at the desired value.

The circulation system was constituted by the strong solution vessel, a collecting tank, and a circulation pump. The strong solution vessel was maintained in an acrylic water bath of which the temperature was controlled by an external bath circulation within ±0.1 K. The solution pump delivered the strong solution to the top of the absorber at a volumetric known flow rate. A metering pump (Watson-Marlow 313-S), previously calibrated, allows us to maintain a fixed flow rate with less than 0.1 K. The solution pump delivered the strong solution at a volumetric known flow rate. A metering pump (Watson-Marlow 313-S), previously calibrated, allows us to maintain a fixed flow rate with less than 0.1 K. The solution pump delivered the strong solution to the top of the absorber using the solution pump. Inside the inner tube, a nonstructural packing of glass raschig rings was used to favor the contact between the strong solution and the vapor refrigerant. The characteristics of the packing material are shown in Table 1. A 0.5 L spherical Pyrex vessel was used as an evaporator device. The heat of vaporization was provided by means of an electrical heater. The absorption temperature was maintained at a fixed value using a thermostatic bath. It can provide a flow rate of up to 160 kg/h, which is sufficient to maintain the temperature at the desired value.

The experimental conditions and geometry of the absorption column and packing are listed in Table 1. A 0.5 L spherical Pyrex vessel was used as an evaporator device. The heat of vaporization was provided by means of an electrical heater. The absorption temperature was maintained at a fixed value using a thermostatic bath. It can provide a flow rate of up to 160 kg/h, which is sufficient to maintain the temperature at the desired value.

The experimental procedures are as follows. The working fluids (strong solution) were introduced into the solution chamber, that was equipped with an electrical heater and a controller (±0.1 K). The solution chamber, evaporator, sampling device, and reservoir were evacuated to the required vacuum level. The water vapor was generated by controlling the evaporator temperature and pressure. The temperature of the absorber in the absorption refrigeration machine).
The vapor pressures of mixtures measured at various concentrations in the range of temperature from 293.15 to 343.15 K are listed in previous papers of this research group.\textsuperscript{17,18} The vapor pressures of mixtures proposed are smaller than that of LiBr, so that the driving potential increases and improves the absorption capacity of absorption refrigeration system with LiBr. But this factor alone does not justify the observed differences in absorption capacity between the mixtures. Formate mixtures with similar vapor pressures to those of the other salts exhibit a better mass transfer behavior used in the same concentration. The enhancement of the mass transfer that these organic salts produce could be due to a higher surfactant ability of these salts. In a follow-up work, the influence of the surface tension on the mass transfer will be experimentally evaluated.

Absorption data for lithium bromide solutions at different concentrations of salt at the top of the absorber were measured at the same absorbent flow rate. Figure 3 shows the total amount of water vapor absorbed by these solutions (eq 2) versus absorbent concentration.

\[
\text{absorbed amount of water} = M_{\text{abs}} t_{\text{abs}} \text{ g} \tag{2}
\]

where \(M_{\text{abs}}\) was calculated by eq 1, and \(t_{\text{abs}}\) (h) is the duration of the absorption experiment (3 min).

The water vapor absorbed increases exponentially with absorbent flow rate, so the maximum absorption rate is reached near a value next to the solubility limit of the salt. The solubility limits must accommodate the working conditions to avoid the crystallization of the salt in the absorber.

The experimental results for the selected systems LiBr + CH\(_2\)CO\(_2\)Na (sodium formate) + water, LiBr + CH\(_2\)CO\(_2\)K (potassium formate) + water, CH\(_2\)CO\(_2\)Na (sodium formate) + water, and CH\(_2\)CO\(_2\)K (potassium formate) + water solutions are graphically presented in Figures 4 and 5. The pure LiBr solution is included for comparison. The pure organic salt solutions present a great absorption capacity, higher than lithium bromide solutions in similar concentrations. The disadvantage of the organic salts is their low solubility that does not enable the use of concentrations above 30%.

In order to provide the thermodynamic design data for absorption refrigeration machines, a computer software described in a previous paper\textsuperscript{16} is used to simulate the performance of absorption systems. The computer program analyzes the thermodynamic reference cycle and evaluates the heat exchanges, temperatures around the cycle, and efficiency. By means of the program, the efficiency of absorption cycle can be evaluated, that enables comparison of different refrigeration cycles. The influence of the input variables in the cycle is also evaluated. The program structure and the mass and energy balances at each part of the absorption cycle were described in this previous work.\textsuperscript{16} The physical properties of the mixtures are also reported in previous works of the group.\textsuperscript{17,18}

Figure 6 and Figure 7 show the absorption refrigeration cycles of the selected systems. By means of the program, one refrigeration cycle with an absorbent actually used in industry (lithium bromide) and another cycle with the absorbent studied in this investigation (lithium bromide–salt mixture) were simulated. The results of the simulation are reported in Table 4.

<table>
<thead>
<tr>
<th>vapor pressure (kPa)</th>
<th>water (refrigerant)</th>
<th>LiBr, 30%</th>
<th>LiBr + CH(_2)CO(_2)Na, 30%</th>
<th>LiBr + CH(_2)CO(_2)K, 30%</th>
<th>LiBr + CH(_3)CH(OH)CO(_2)Na, 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.37</td>
<td></td>
<td>5.62</td>
<td>4.90</td>
<td>5.10</td>
<td>5.00</td>
</tr>
</tbody>
</table>

Figure 3. Influence of absorbent concentration in absorption rate.

Figure 4. Absorption of water vapor into new working fluids. (■) LiBr + water solution, (○) LiBr + CH\(_2\)CO\(_2\)Na + water solution, (▲) CH\(_2\)CO\(_2\)Na + water solution.

Figure 5. Absorption of water vapor into new working fluids. (■) LiBr + water solution, (○) LiBr + CH\(_2\)CO\(_2\)K + water solution, (▲) CH\(_2\)CO\(_2\)K + water solution.
Conclusion

Four different working fluids LiBr + CHO₂Na (sodium formate) + water, LiBr + CHO₂K (potassium formate) + water, LiBr + CH₃CO₂K (potassium acetate) + water, and LiBr + CH₃CH(OH)CO₂Na (sodium lactate) + water solutions were chosen and examined for comparison. In preliminary absorption experiments, the absorption rate of the mixtures LiBr + CH₃CO₂K (potassium acetate) + water, and LiBr + CH₃CH(OH)CO₂Na (sodium lactate) + water solution are lower than that of LiBr + water solution, at the same total concentration of salt.

Among these four working fluids, the LiBr + CHO₂Na (sodium formate) + water solution was confirmed to have a better absorption capacity than the lithium bromide alone, so that this absorbent is a promising candidate for an absorption chiller, considering the operation range, because its mass transfer characteristics were comparable with the LiBr + water solutions.

Acknowledgment

This work was supported by Enermes S.A.

Literature Cited


*Received for review* September 19, 2006

*Revised manuscript received* October 20, 2006

*Accepted* October 24, 2006

IE061229B