Electrical conductivity of concentrated LiBr Ethylene-Glycol and water ternary system

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Abstract. LiBr/H₂O as working pair in absorption chiller is widely used in the absorption refrigeration system, and the electrical conductivity is used as secondary properties as an empirical relation with temperature and concentration as a simple method to measure the concentration. In this paper, another working pair Carrol/H₂O is chosen, more suitable for air-cooled cycles. Carrol contains ethylene glycol and LiBr with a mass ratio at 4.5:1 and has advantages of low risk of crystallization and reduce the LiBr charge. The working range for the LiBr/H₂O solution is temperature 25-80ºC, at concentration 50–64%, in term of Carrol/H₂O system, the temperature range is 25-80ºC, concentration range is 50%-75%. The electrical conductivity will be measured according to the working range and a typical used solution extracted from an absorption chiller prototype will also be measured to compare with the experimental result.

1. Introduction

LiBr is currently a widely used absorbent in the absorption chiller and the measurement of concentration of the working pairs in the chiller is often required. Several methods could be employed like Coriolis flow meter, titration method, in which titration method could not be applied to a working process and Coriolis flow meter is generally expensive, difficult in maintenance and space cost. Hence the electrical conductivity, which is a function of temperature and concentration could be used as a secondary property to measure the concentration indirectly. In the case of direct air-cooled cycles, the use of LiBr as absorbent is limited due to problems of crystallization [1]. Carrol contains ethylene glycol and LiBr with a mass ratio at 4.5:1 and has advantages concerning crystallization due to higher solubility [2], moreover the LiBr charge is reduced.

The electrical conductivity (EC) whose unit is mS/cm, or electrical resistivity in mmho/cm, is the ability of the solution of conducting a current. With the increase of temperature of the solution, the EC will increase due to the ionization of molecules, which will increase the ion density in the volume [3]. But due to the ionization process, the ion density and mobility is not always reflecting the direct proportion relationship. Though the electrical conductivity could be a critical parameter to determine the concentration of the solution of an alternative way in a continuous process, only a few literatures described the experimental data and theory. And about the Carrol aqueous solution, according to the author’s knowledge, there is no literature about it.

Frled [4] shows the electrical resistivity of concentrated LiBr aqueous solutions at LiBr mass ratio 40-63%, at temperature range 15-80ºC, the absolute accuracy of analytical determination is ±0.7% at concentration 40-50%.

De Diego [5] did experiments that included LiBr and fitted the experimental results to the Falkenhagen equation at 25ºC.

Sun [6] measured electrical resistivity of LiBr aqueous solution at 10-100ºC temperature range, and concentrations at 35-70wt%, and the measurements were reproducible with 1 mmho and the regression was done into a polynomial correlation.

Osta-Omar [7] measured the electrical conductivity of LiBr/water solution from 25ºC -95ºC at a concentration range 45-65%. The maximum error with experiment data and the fitted equation is 5.8%.
Labra [8] did research about the determination of the concentration for a prototype absorption machine, in which electrical conductivity was at the range of 35-80°C for temperature and 45-65wt% for concentration. Refractive index, density, sound velocity, and considered the method of measurement of properties of working fluids used in the prototypes of absorption due to its low cost, easy installation, and small volume needed for the measurement.

2. Experiment Set up for electrical conductivity
During the experiment of electrical conductivity measurement, the solution sample should be well prepared to decrease uncertainty, and temperature, ion density should be uniform in the sample. As shown in Figure 1, sensor 5 is an electrode to measure electrical conductivity with accuracy at 0.5% and a temperature sensor integrated. Also, to avoid the stratification of different organic/inorganic group and ions, a stirring machine 3 is used to stir the solution, 4 is the magnetic stick to stir the solution sample. 6 are PT100 temperature sensors with error ±0.03°C to measure the temperature of different points in solution and 7 are thermal couples to control the surrounding temperature, 8 are thermal blankets to heat the whole system. 2 is a data acquisition machine and 9 is the control computer.

The LiBr used with purity > 99%, Ethylene Glycol with a purity > 99%. The solution is prepared with a balance at an accuracy of 0.01g and the density will be measured with a densimeter. For each case, the solution sample will be sealed with a rubber tap to avoid the potential evaporation and absorption in the heating or cooling process. The experiment result is reproducible within 1 mS/cm.

![Figure 1. Experiment scheme of conductivity measurement](image)

3. Experiment result and analysis
For each measurement, the data must be waited a short minute to be recorded to avoid latencies of the sensor. As shown in Figure 2, the electrical conductivity will increase along with the temperature at the same concentration and will also decrease with concentration at the same temperature. One of the key points that the electrical conductivity could be used to measure the concentration is the high linearity when the concentration or the temperature changes.
In Figure 3, the result is compared with experimental data from [4][6][8], at three temperature, 35, 50, 70 ºC, for better visualization. The maximum of the average absolute deviation of the electrical conductivity is shown in Table 1. The discrepancy from different authors could be caused by various factors, such as the purity of the material, the accuracy of the balance, relative error of the electrode and the preparation procedure, etc.

Table 1. Deviation between different authors and this work

|       | 54% | 56% | 58% | 60% | 62% |
|-------|-----|-----|-----|-----|-----|
| Frled[4] | 6.2% | 3.2% | 0.8% | 1.6% | 3.7% |
| Sun[6]  | 5.7% | 3.4% | 1.6% | 1.3% | 4.5% |
| Labra[8] | 2.2% | 7.9% | 6.4% | 3.7% | 4.1% |

Figure 4 shows the experimental results of the electrical conductivity of Carrol solution at various concentration and temperature. From which it could be observed that the electrical conductivity of the Carrol solution is
lower than the LiBr solution at the same ratio of electrolyte due to the presence of organic component. While the linear relationship remains the same for the Carrol solution.

For the LiBr and Carrol aqueous solution, an empirical relation with temperature, electrical conductivity and concentration are shown as equation (1).

\[
C = A_0 + A_1T + A_2T^2 + A_3T^3 + B_1EC + B_2EC^2 + B_3EC^3 + C_1T^*EC + C_2T^*EC^2 + C_3T^*EC^3
\]  
(1)

Where the corresponding coefficients of the equation is shown in Table 2.

|                   | A0   | A1   | A2   | A3   | B1   | B2   | B3   | C1   | C2   | C3   |
|-------------------|------|------|------|------|------|------|------|------|------|------|
| LiBr solution     | 69.6778 | 0.49565 | -6.66E-03 | 7.49E-05 | -0.25783 | 3.06E-04 | -2.85E-06 | 2.42E-03 | 1.71E-05 | -5.58E-05 |
| Carrol solution   | 69.6581 | 0.29348 | -2.61E-03 | -2.05E-04 | -0.18627 | -1.52E-05 | 4.48E-06 | 2.21E-03 | -4.93E-05 | 1.69E-04 |

\(C\) is the concentration of solute %, \(EC\) is the electrical conductivity of mS/cm, \(T\) is the temperature of the solution of °C. The expanded uncertainty of the mass fraction of the solution is 0.8%, and for the electrical conductivity of Carrol, LiBr aqueous solution are ±0.3%, ±0.4%, respectively.

4. Conclusion

The experimental result of both aqueous solutions shows a max discrepancy of 6.2% when compared with other authors. The high linearity shows the possible replacement with EC electrode to the mass flowmeter. As shown in Table 1, the equation shows the relationship between temperature, EC and concentration. The average error between empirical equation and the experimental result is 0.25% and 0.3% at Carrol and LiBr aqueous solution.

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