Solid – Liquid Equilibria (SLE) 
and 
Vapour – Liquid Equilibria (VLE) 
of 
Aqueous LiBr 

Zurich, June 2014
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Introduction

Aqueous electrolyte solutions, as liquid desiccants in air conditioning applications, have been known and widely tried since the 1930s. They are characterized by two fundamental properties: – A high affinity for water, and their high corrosion potential of most technical metals and alloys. In the past few years, serious attempts have been made to evade the corrosion problem by replacing metals with polymers on all surfaces that might come into contact with those electrolyte solutions. Electrolyte solutions are also frequently transported as aerosols when they come into contact with moving air, and cause corrosion as well in parts of the equipment and air conditioning plants, that, theoretically, do not have to come in contact with them. As it so often happens in technical fields, the most effective liquid desiccants are the most corrosive ones as well. On the other hand, if an effective, and economically acceptable solution of the corrosion problem can be found, the most efficient desiccants ought to be preferred in order to maximize energy efficiency, and thus, minimize the degradation of resources.

Among the aqueous electrolyte solutions with the highest water affinity, are sulphuric acid, sodium hydroxide, and the chlorides of lithium, calcium and magnesium, as well as the bromide and iodide of lithium.

This report presents methods of calculation for SLE and VLE of aqueous lithium bromide (LiBr – H₂O) from the point of view of air dehydration applications. In a companion report SLE and VLE calculation methods are for aqueous NaOH are presented as well. Earlier published reports covered in detail the properties of the lithium and calcium chloride.

Solid – Liquid Equilibria of Aqueous LiBr

The solubility boundary of LiBr in water has been the subject of many studies, carefully summarized by Pátek and Klomfar. For the SLE boundary we adopt here the solution of these authors, and reproduce it for the sake of completeness. The equation for the saturation temperature on the SLE line is

\[ T(x) = T_L + \frac{T_R - T_L}{x_R - x_L}(x - x_L) + T_L\sum_{i=1}^{N}a_i(x - x_L)^{m_i}(x_R - x)^{n_i} \tag{1} \]

where \( x \) is the mole fraction of the solute. \( T_L \) and \( T_R \) are the temperatures at the limits of a given region of the SLE boundary, and \( x_L \) and \( x_R \) are the mole fractions at the same limits.

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The mole fraction of the solute and its mass fraction in solution are related by

\[ x = \frac{\xi}{\xi + \frac{M_{LiBr}}{M_{H_2O}}(1 - \xi)} = \frac{\xi}{\xi + 4.8209108(1 - \xi)} \]  

(2)

The parameters of equation (1) are given in Table 1 for the various segments of the SLE Curve, (see Figure 1).

**Table 1 – Parameters of equation (1) for the five (5) segments of the SLE Curve.**

<table>
<thead>
<tr>
<th>i</th>
<th>(a_i)</th>
<th>(m_i)</th>
<th>(n_i)</th>
<th>(T_L)</th>
<th>(T_R)</th>
<th>(x_L)</th>
<th>(x_R)</th>
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**A – B Line**

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<th>(T_R)</th>
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<th>(x_R)</th>
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**C – D Line**

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**D – E Line**

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</table>
**Stable Transition Points**

- $\xi_A = 0.390$ 941
- $\xi_B = 0.479$ 439
- $\xi_C = 0.578$ 070
- $\xi_D = 0.659$ 816

**Figure 1** - The SLE Curve for aqueous LiBr.
Vapour–Liquid Equilibria of Aqueous LiBr

The vapour–liquid equilibria of aqueous LiBr has been the subject of numerous studies3,4,5,6,7,8,9,10,11,12,13, particularly concerned with the use of this solution absorption refrigeration equipment. Some of these studies were eminently practical (e.g. Pennington and McNeely) while a few others sought a more theoretical approach (e.g. Herold and Moran8, or, Peters and Keller10).

Feuerecker9, as well as Loewer4 before, carried out measurements of the vapour pressure of aqueous LiBr and proposed equations for its calculation as function of temperature and a measure of concentration. Both applied the Duehring rule as a tool with more or less success in terms of covering all the regions of interest. Feuerecker limited the application of the Duehring rule to solute mass fractions above 0.40, and suggested interpolating at lower mass fractions, without proposing any method.

3 Pennington, W. 1955. How to find accurate vapor pressures of LiBr water solutions, Refrigerating Engineering, 63(5), 57-61.
In this report we propose the use of the Feuerecker solution, with an extension at mass fractions below 0.40 based on a method proposed by Hoffmann and Florin. The work of Hoffmann and Florin is part of an effort to obtain diagrams allowing for simple and sufficiently accurate graphical interpolation, as needed in practice at the time. In fact, they propose to use a modified temperature scale that transforms the graph of the vapour pressure of aqueous solutions at constant composition into a straight line:

$\log P_v = a + b \frac{1}{\tau}$  \hspace{1cm} (3)

where $\tau$ represents the modified temperature scale defined as

$$\frac{1}{\tau} = \frac{c_1}{T} + c_2 + c_3 \log T + c_4 T$$  \hspace{1cm} (4)

The straight lines generated by this method are not parallel. Their intercepts $a$ and slopes $b$ are functions of the solute mass fraction. The $c_i$ coefficients are given by Hoffmann and Florin for pressures in mmHg, in Table 2.

**Table 2 – Coefficients of the Hoffmann and Florin equation (4).**

<table>
<thead>
<tr>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$c_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>$-7.9151 \times 10^{-3}$</td>
<td>$2.6726 \times 10^{-3}$</td>
<td>$-0.8625 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The intercepts $a$ and slopes $b$ at constant solute mass fractions, were determined from data in the literature, and adimensionalized as

$$\alpha \equiv \frac{a}{a_{\xi=0.0}} \quad \beta \equiv \frac{b}{b_{\xi=0.0}}$$  \hspace{1cm} (5)

$a$ and $\beta$ were plotted as depicted in Figure 2, and suitable functions established that represent both parameters adequately in the range of interest, $0.0 \leq \xi \leq 0.60$.

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Figure 2 - Dimensionless intercept and slope of the Hoffmann and Florin vapour pressure equation for aqueous LiBr.
The equations for intercept and slope of the vapour pressure lines in the solute mass fraction range $0.0 \leq \xi \leq 0.60$ have the same form, equation (6):

$$\alpha(\xi) = a_4 \xi^5 + \sum_{i=0}^{3} a_i \xi^i$$

$$\xi_r = \frac{\xi - \xi_s}{1 - \xi_s}$$

Finally, the vapour pressure $P_v(T, \xi)$ [kPa] is calculated as

$$P_v = 0.13332 \cdot 10^{\alpha(\xi) + \beta(\xi)}$$

with the parameters for equations (6) and (7) given in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_0$</th>
<th>$\beta_0$</th>
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<tr>
<td>Intercept</td>
<td>1.0</td>
<td>-0.020666</td>
<td>-0.033163</td>
<td>0.023244</td>
<td>4.434134 $\times 10^{-4}$</td>
<td>7.023440338</td>
<td>-</td>
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<tr>
<td>Slope</td>
<td>1.0</td>
<td>3.996784 $\times 10^{-3}$</td>
<td>-5.547374 $\times 10^{-4}$</td>
<td>0.074209</td>
<td>-0.011838</td>
<td>-</td>
<td>-3146.761589</td>
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</tbody>
</table>

A method based on the Duehring rule is used for solute mass fractions larger than 0.40, as proposed by Feuerecker. The Duehring rule says that a plot of a solution (S) temperature versus the dew-point temperature of the solvent, (w), is a straight line, thus

$$T_S = A + B \cdot T_{DP,w} \quad \Rightarrow \quad T_{DP,w} = \frac{T_S - A}{B}$$

where the intercept $A$ and the slope $B$ are functions of a measure of the solute concentration, e.g. mass fraction $\xi$ or mole ratio $\mu$. The mole ratio is defined as

$$\mu = \frac{M_w}{M_s} \cdot \frac{\xi}{1 - \xi}$$
The $A$ and $B$ functions of $\mu_i$ are given by

$$
A = \sum_{i=0}^{4} A_i \cdot \mu_i^i \quad \quad B = \sum_{i=0}^{4} B_i \cdot \mu_i^i
$$

(10)

with the $A_i$ and $B_i$ coefficients given in Table 4.

**Table 4** - Parameters for equations (10).

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>$B$</td>
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<td>6.70042</td>
<td>-15.42090</td>
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</tr>
</tbody>
</table>

Finally, the vapour pressure is calculated from the dew point temperature $T_{DP,w}$ with the IAPWS\textsuperscript{16} equation, for example:

$$
\ln \left( \frac{p}{p_c} \right) = \frac{T_c}{T_{DP,w}} \left( a_1 \tau + a_2 \tau^{1.5} + a_3 \tau^3 + a_4 \tau^{3.5} + a_5 \tau^4 + a_6 \tau^{7.5} \right)
$$

(11)

$$
\tau = 1 - \frac{T_{DP,w}}{T_c}
$$

with the coefficients $a_\phi$

$$
\begin{align*}
    a_1 &= -7.85951783 & a_2 &= 22.6807411 \\
    a_3 &= 1.84408259 & a_4 &= -15.9618719 \\
    a_5 &= -11.7866497 & a_6 &= 1.80122502
\end{align*}
$$

and the critical constants:

$$
T_c = 647.096 \text{ K} \quad \quad p_c = 22.064 \text{ MPa.}
$$

An Othmer Chart created with the described model is depicted in Figure 3 below.

\textsuperscript{16} The International Association for the Properties of Water and Steam, Revised Supplementary Release on the Properties of Ordinary Water Substance, St. Petersburg - Russia, 1992.
Figure 3 - An Othmer Diagram of aqueous LiBr.