



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

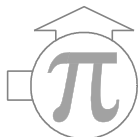
Zurich, June 2014



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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 chloride¹.

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 Klomfar². 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

$$T(x) = T_L + \frac{T_R - T_L}{x_R - x_L} (x - x_L) + T_i \sum_{i=1}^N a_i (x - x_L)^{m_i} (x_R - x)^{n_i} \quad (1)$$

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.

¹ Conde, M. R. 2004. Properties of aqueous solutions of lithium and calcium chlorides: Formulations for use in air conditioning equipment design, Int. J. of Thermal sciences, 43, 367 - 382.

² Pátek, J., J. Klomfar 2006. Solid–liquid phase equilibrium in the systems of LiBr–H₂O and LiCl–H₂O, Fluid Phase Equilibria, 250, 138–149.

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

$$x = \frac{\xi}{\xi + \frac{M_{LiBr}}{M_{H_2O}}(1 - \xi)} = \frac{\xi}{\xi + 4.8209108(1 - \xi)} \quad (2)$$

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.

<i>Ice Line</i>							
<i>i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>T_L</i>	<i>T_R</i>	<i>x_L</i>	<i>x_R</i>
1	13.3842	1	1	273.16	202.8	0.0	0.1175
2	-43.9293	2	1				
3	4025.77	3	1				
4	-55236.4	4	1				
5	328383.0	5	1				
<i>A - B Line</i>							
1	26.1161	1	1	202.8	222.4	0.1175	0.1604
2	23899.4	1	3				
<i>B - C Line</i>							
1	24.7039	1	1	222.4	277.1	0.1604	0.2213
2	4654.59	1	3				
<i>C - D Line</i>							
1	16.2375	1	1	277.1	322.2	0.2213	0.2869
2	2470.98	1	3				
<i>D - E Line</i>							
1	10.0743	1	1	322.2	429.15	0.2869	0.4613
2	3945.93	1	4				

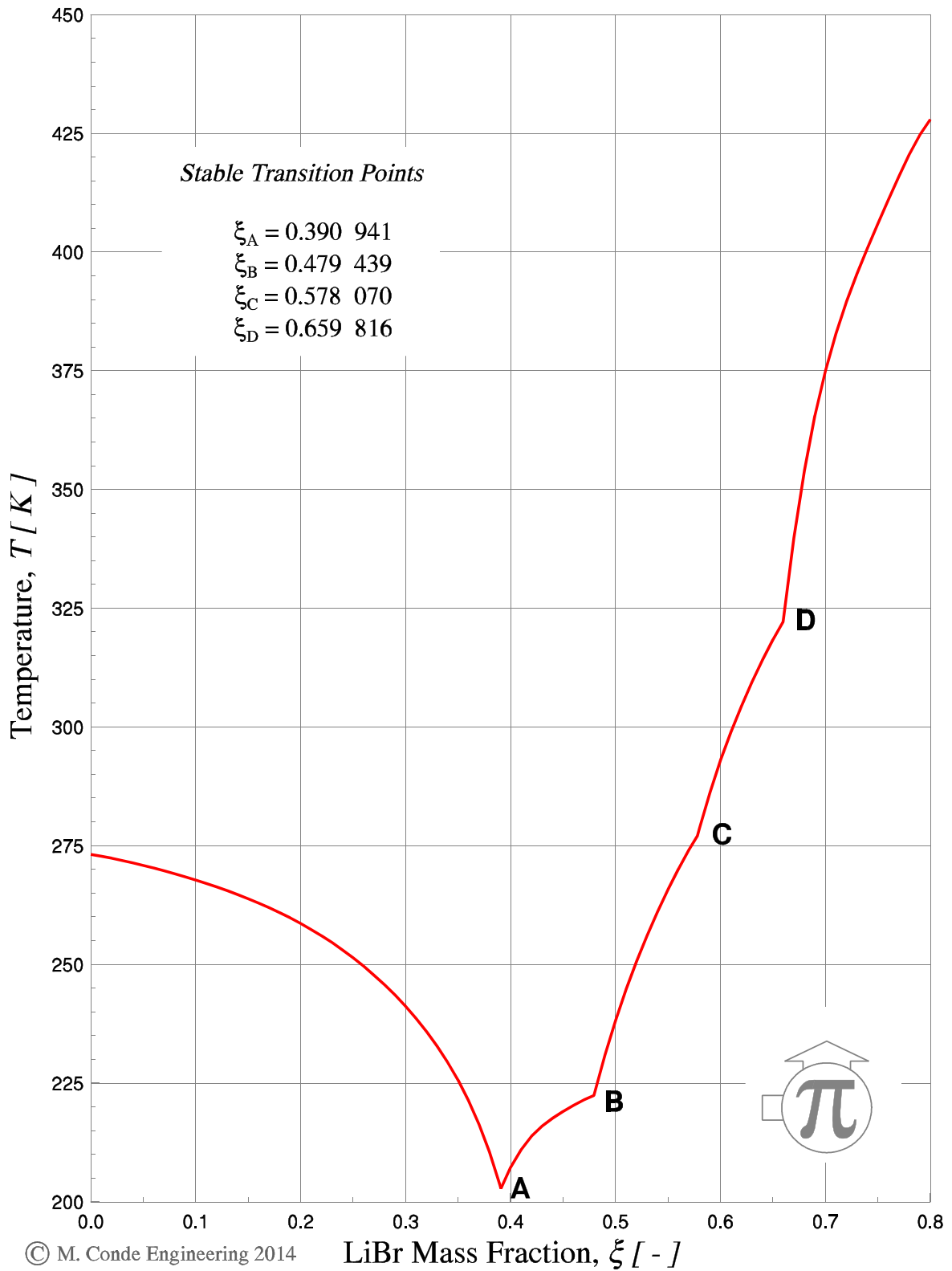


Figure 1 - The SLE Curve for aqueous LiBr.

Vapour – Liquid Equilibria of Aqueous LiBr

The vapour – liquid equilibria of aqueous LiBr has been the subject of numerous studies^{3,4,5,6,7,8,9,10,11,12,13}, 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 Dühring rule as a tool with more or less success in terms of covering all the regions of interest. Feuerecker limited the application of the Dühring rule to solute mass fractions above 0.40, and suggested interpolating at lower mass fractions, without proposing any method.

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- ³ Pennington, W. 1955. How to find accurate vapor pressures of LiBr water solutions, *Refrigerating Engineering*, 63(5), 57-61.
 - ⁴ Loewer, H. 1960. *Thermodynamische und physicalische Eigenschaften der waesserigen Lithiumbromid-Loesung*, Dissertation, Technische Hochschule Karlsruhe.
 - ⁵ McNeely, L. A. 1979. Thermodynamic properties of aqueous solutions of lithium bromide, *ASHRAE Transactions*, 85/1, 413-434.
 - ⁶ Renz, M. 1981. *Bestimmung thermodynamischer Eigenschaften waessriger und methylalkoholischer Salzloesungen*, Dissertation, Universitaet Essen.
 - ⁷ Brunk, M. F. 1982. *Thermodynamische und physikalische Eigenschaften der Loesung Lithiumbromid/Wasser als Grundlage fuer die Prozeßsimulation von Absorptions-Kaelteanlagen*, *Ki Klima - Kaelte - Heizung*, 10, 365-372.
 - ⁸ Herold, K. E., M. J. Moran 1987. Thermodynamic properties of lithium bromide/water solutions, *ASHRAE Transactions*, 93/1.
 - ⁹ Feuerecker, G. 1994. *Entropieanalyse fuer Waermepumpensysteme: Methoden und Stoffdaten*, Dissertation, Technischen Universitaet Muenchen.
 - ¹⁰ Peters, R., J. U. Keller 1994. Solvation model for VLE in the system H₂O–LiBr from 5 to 76 wt%, *Fluid Phase Equilibria*, 94, 129-147.
 - ¹¹ Murakami, K., H. Sato, K. Watanabe 1995. A new bubble-point-pressure correlation for the binary LiBr/H₂O solution, *Int. J. Thermophysics*, 16(3), 811-820.
 - ¹² Chua, H. T. et al. 2000. Improved thermodynamic property fields for LiBr–H₂O solution, *Int. J. Refrigeration*, 23, 412-429.
 - ¹³ Yuan, Z., K. E. Herold 2005. Thermodynamic Properties of Aqueous Lithium Bromide Using a Multiproperty Free Energy Correlation, *HVAC&R Research*, 11(3), 377-393.

In this report we propose the use of the Feuerecker⁹ solution, with an extension at mass fractions below 0.40 based on a method proposed by Hoffmann and Florin¹⁴. 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:

$$\log Pv = a + b \frac{1}{\tau} \quad (3)$$

where τ represents the modified temperature scale defined as

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

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 Florin¹⁴ for pressures in *mmHg*, in Table 2.

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

c_1	c_2	c_3	c_4
1.0	-7.9151×10^{-3}	2.6726×10^{-3}	-0.8625×10^{-6}

The intercepts a and slopes b at constant solute mass fractions, were determined from data in the literature^{4,5,6,15}, and adimensionalized as

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

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

¹⁴ Hoffman, W., F. Florin 1943. Zweckmaessige Darstellung von Dampfdruckkurven, Z. VDI - Beiheft Verfahrenstechnik, 2, 47-51.

¹⁵ Boryta, D. A., A. J. Maas, C. B. Grant 1975. Vapor Pressure-Temperature-Concentration Relationship for System Lithium Bromide and Water (40 - 70% Lithium Bromide), J. Chem.Eng. Data, 20(3), 316-319.

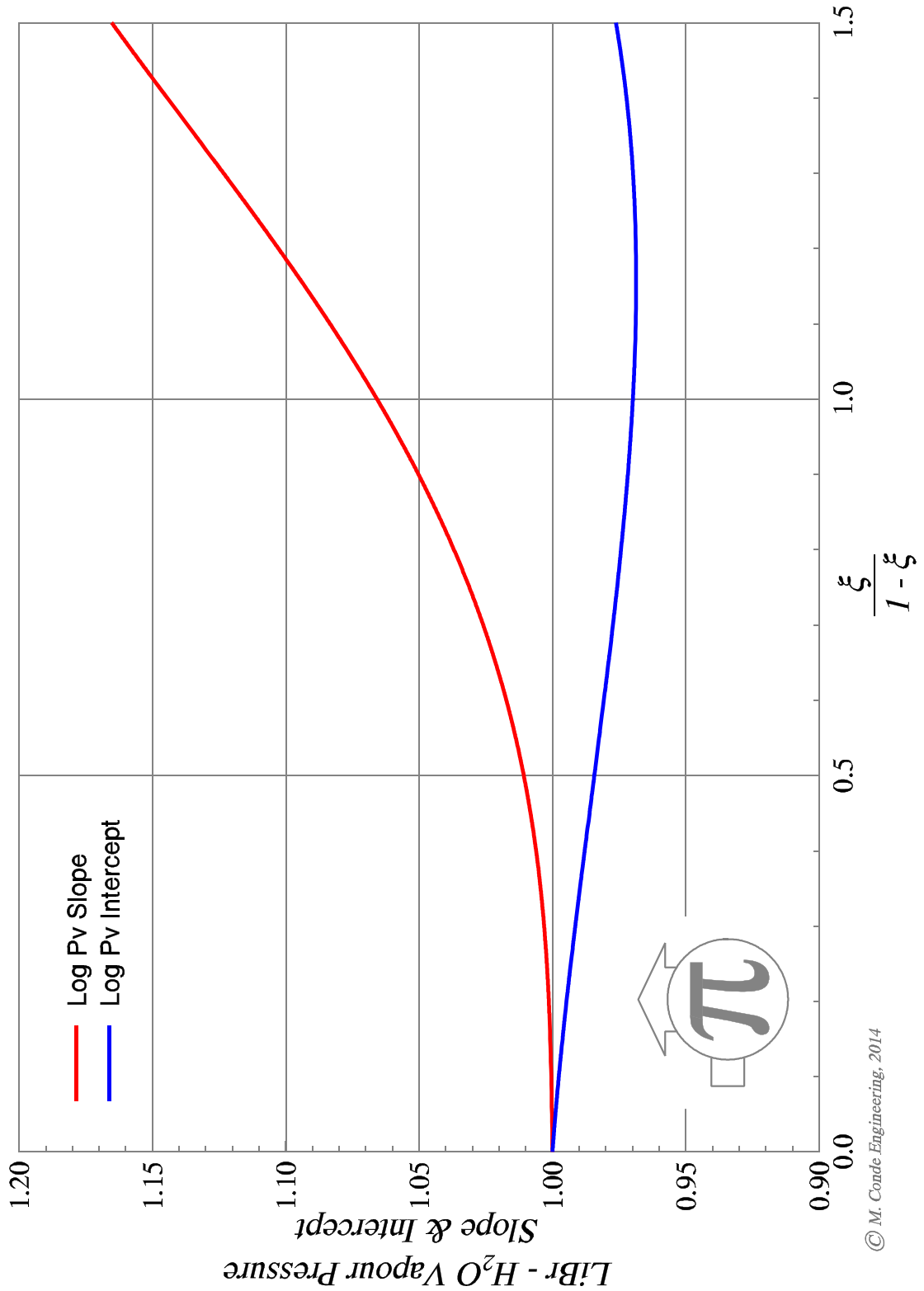


Figure 2 - Dimensionless intercept and slope of the Hoffmann and Florin vapour pressure equation for aqueous LiBr.

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):

$$\alpha(\xi) = a_4 \xi_r^5 + \sum_{i=0}^3 a_i \xi_r^i \quad (6)$$

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

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

$$P_v = 0.13332 \cdot 10^{\alpha_0 \cdot \alpha(\xi) + \frac{\beta_0 \cdot \beta(\xi)}{\tau(T)}} \quad (7)$$

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

Table 3 – Parameters for equations (6) and (7).

	a_0	a_1	a_2	a_3	a_4	α_0	β_0
Intercept	1.0	-0.020666	-0.033163	0.023244	$4.434134 \cdot 10^{-4}$	7.023440338	-
Slope	1.0	$3.996784 \cdot 10^{-3}$	$-5.547374 \cdot 10^{-4}$	0.074209	-0.011838	-	-3146.761589

A method based on the Duehring rule is used for solute mass fractions larger than 0.40, as proposed by Feuerrecker⁹. 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

$$T_S = A + B \cdot T_{DP,w} \quad \Rightarrow \quad T_{DP,w} = \frac{T_S - A}{B} \quad (8)$$

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

$$\mu \equiv \frac{M_w}{M_s} \cdot \frac{\xi}{1 - \xi} \quad (9)$$

The A and B functions of μ , are given by

$$A = \sum_{i=0}^4 A_i \cdot \mu^{\frac{i}{2}} \quad B = \sum_{i=0}^4 B_i \cdot \mu^{\frac{i}{2}} \quad (10)$$

with the A_i and B_i coefficients given in Table 4.

Table 4 - Parameters for equations (10).

	0	1	2	3	4
A	340.897	-2638.978	7262.473	-8119.078	3302.087
B	-0.01050	6.70042	-15.42090	16.42477	-6.34249

Finally, the vapour pressure is calculated from the dew point temperature $T_{DP,w}$ with the IAPWS¹⁶ equation, for example:

$$\ln\left(\frac{p}{p_c}\right) = \frac{T_c}{T_{DP,w}} \left(a_1 \tau + a_2 \tau^{1.5} + a_3 \tau^3 + a_4 \tau^{3.5} + a_5 \tau^4 + a_6 \tau^{7.5} \right) \quad (11)$$

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

with the coefficients a_p ,

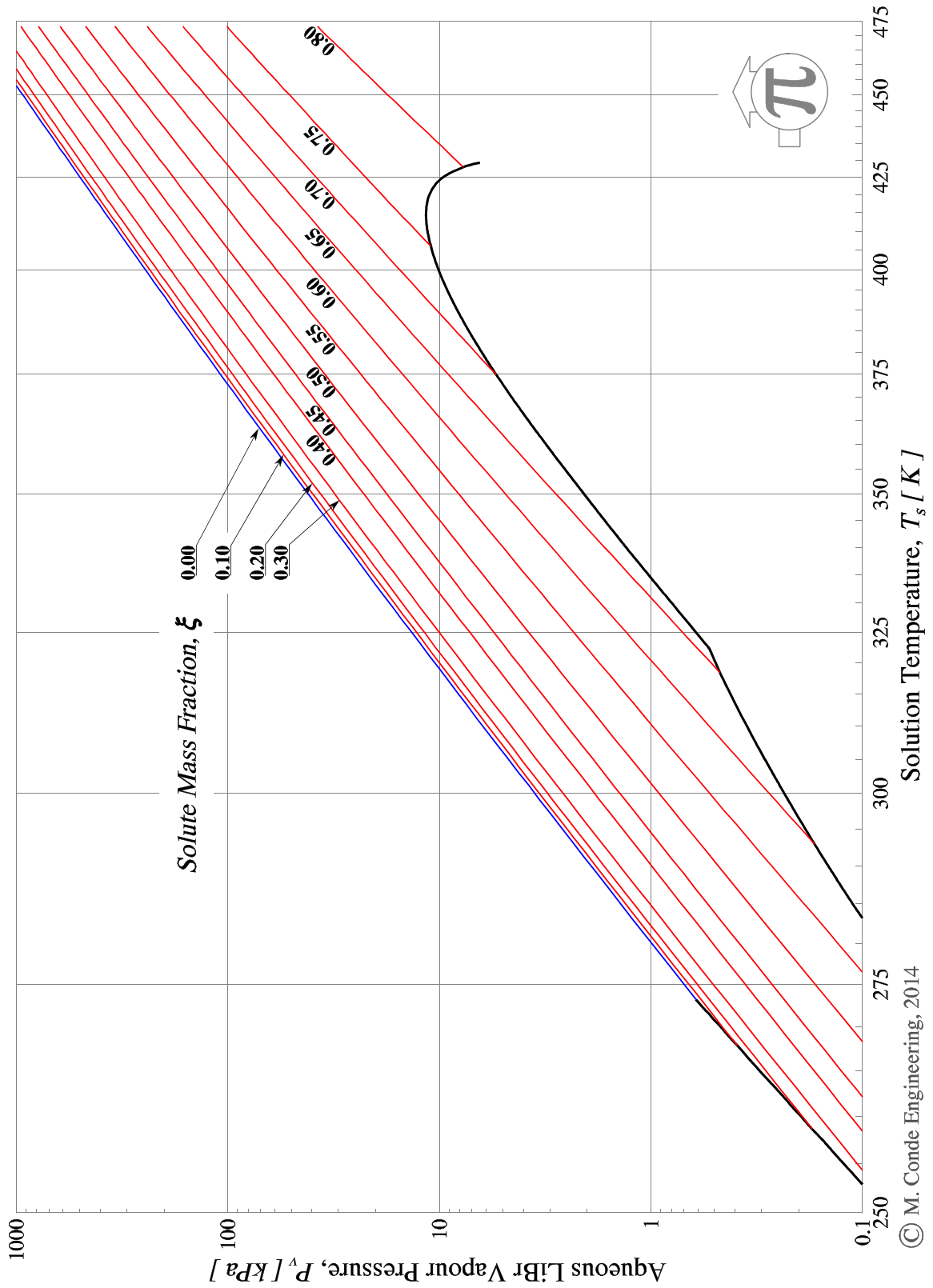
$$\begin{aligned} a_1 &= -7.85951783 & a_4 &= 22.6807411 \\ a_2 &= 1.84408259 & a_5 &= -15.9618719 \\ a_3 &= -11.7866497 & a_6 &= 1.80122502 \end{aligned}$$

and the critical constants:

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

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

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.



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Figure 3 - An Othmer Diagram of aqueous LiBr.