



**Solid – Liquid Equilibrium (SLE)  
and  
Vapour – Liquid Equilibrium (VLE)  
of  
Aqueous NaOH**

Zurich, June 2014



#### **Disclaimer**

This document reports results of our own work, based on results published by others, in the open literature. The author, his firm, and his associates assume no responsibility whatsoever regarding whatever consequences, direct or implied, that may result from their use or misuse.

In no circumstances shall the author, his firm, and his associates be made liable for any losses of profit, or other commercial damages, including, but not limited, to special, incidental, consequential or other damages.



## 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 sodium hydroxide (NaOH - H<sub>2</sub>O) from the point of view of air dehydration applications. A forthcoming report shall do the same for aqueous lithium bromide. Earlier published reports covered in detail the properties of the lithium and calcium chlorides<sup>1</sup>.

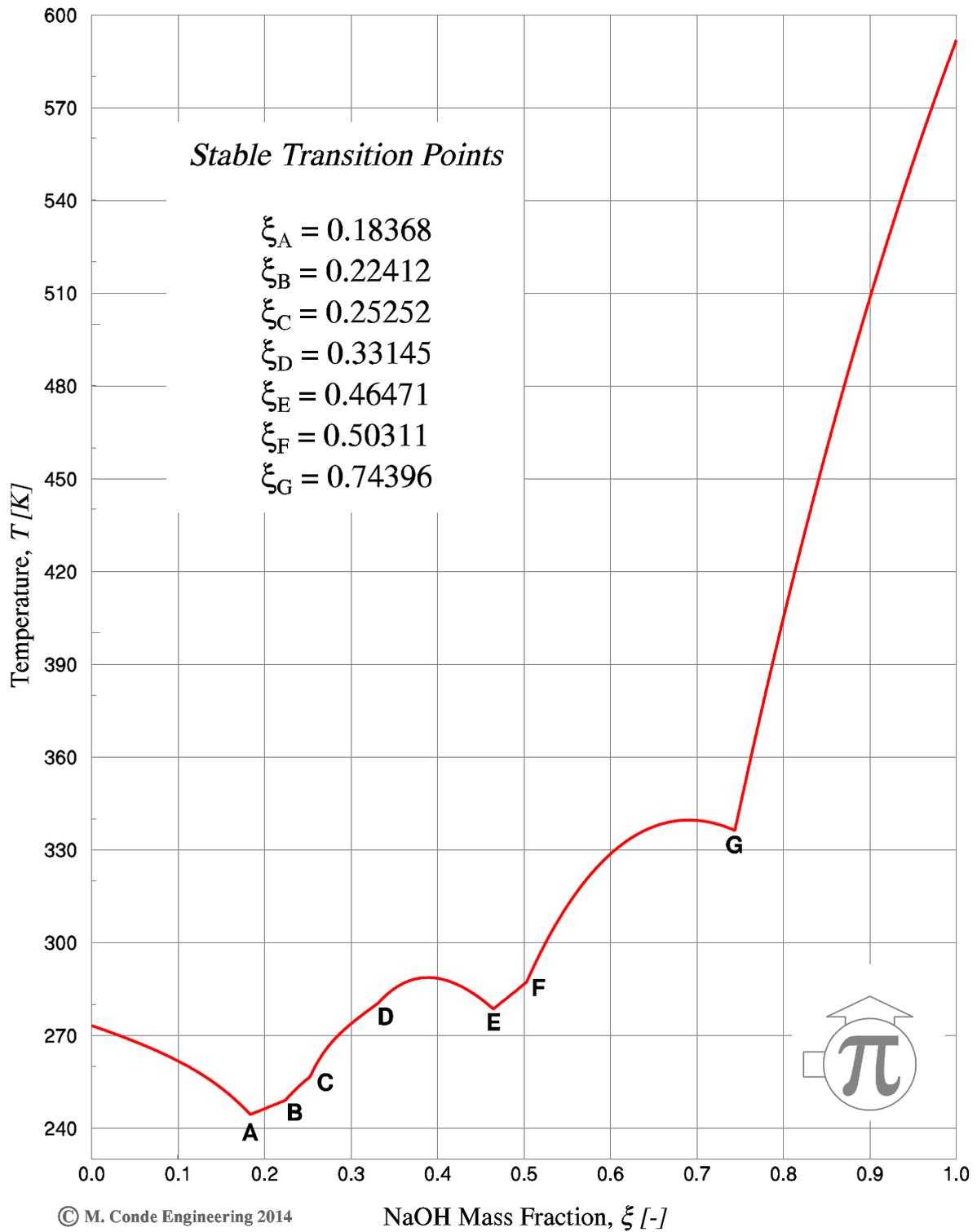
## Solid – Liquid Equilibria of Aqueous NaOH

The solubility boundary of NaOH in water has been extensively studied by Pickering<sup>2</sup> and Braendl<sup>3</sup>, and discussed in detail by Cohen-Adad et al.<sup>4</sup>, Brodale and Giaque<sup>5</sup>, and Murch and Giaque<sup>6</sup> among others. The work of Cohen-Adad et al., settles the accepted solubility boundaries of the various hydrates of sodium hydroxide<sup>7</sup>.

Equations were fitted to the data in these literature sources for the eight (8) segments defining the complete solid – liquid equilibrium line, Figure 1. The equations have the general form

$$T_{SLE} = T_{C,H_2O} \cdot \left( \sum_{i=0}^2 B_i \cdot \xi^i + B_3 \cdot \xi^c \right) \quad (1)$$

The ranges of validity of the equations are defined by the stable transition points as given in Figure 1, and specified in Table 1.



**Figure 1** - The Solid – Liquid Equilibrium line (SLE) and the *Stable Transition Points*. See Table 1 for definition of ranges.

Curves	$B_0$	$B_1$	$B_2$	$B_3$	c	Range
Ice Line	0.422088	-0.147063	-0.231082	-17.238854	4.42	$0.0 \leq \xi \leq 0.18368$
A – B Line	0.345510	0.174967	0.0	0.0	0.0	$0.18368 < \xi \leq 0.224123$
B – C Line	0.221482	0.652784	1.507824	-7.044196	3.2	$0.224123 < \xi \leq 0.25252$
C – D Line	0.51356	-0.701257	1.397530	-1.054578x10 <sup>-6</sup>	-7.5	$0.25252 < \xi \leq 0.33145$
D – E Line	-3.051530	-12.826984	3.288068	12.810284	0.5	$0.33145 < \xi \leq 0.46471$
E – F Line	0.268638	0.348189	0.0	0.0	0.0	$0.46471 < \xi \leq 0.50311$
F – G Line	0.135493	1.557219	-1.299938	-0.026229	-2.5	$0.50311 < \xi \leq 0.74396$
G – H Line	2.814372	0.824233	-0.413355	-2.310897	-0.5	$0.74396 < \xi \leq 1.0$

**Table 1** – Parameters and ranges of validity of the equations of the SLE line.

## Vapour – Liquid Equilibria of Aqueous NaOH

The vapour – liquid equilibria of aqueous NaOH has been studied experimentally by various methods. While von Mural<sup>8</sup> measured the vapour pressure of water over aqueous NaOH for a special purpose, most studies were undertaken for the purpose of filling the knowledge gap<sup>9,10,11,12,13,14,15,16</sup>. Further studies concentrated on modeling along various theories, or simply on a semi-empirical basis, in order to predict the thermophysical properties of aqueous NaOH<sup>17,18,19</sup>.

None of the works cited, or known to us at this point, offers methods to calculate the boundaries, and expedite enough to calculate the water vapour pressure in equilibrium with aqueous NaOH. The empirical model proposed by Krey<sup>14,15</sup> is described in his works as allowing just that. As it happens, although the equations presented in both works are similar, the fifty two (52) coefficients appear in different positions in both works. All attempts with both formulations and sets of coefficients failed to reproduce his own calculated results.

Considering the volume of experimental data available, an approach following the suggestion of Hoffmann and Florin<sup>20</sup> can be applied with success. Hoffmann and Florin proposed plotting the logarithm of the vapour pressure against a modified temperature scale, so as to obtain straight lines at constant mass fractions of the solute.

$$\log P_v = a + b \frac{1}{\tau} \quad (2)$$

$$\frac{1}{\tau} = \frac{c_1}{T} + c_2 + c_3 \log T + c_4 T$$

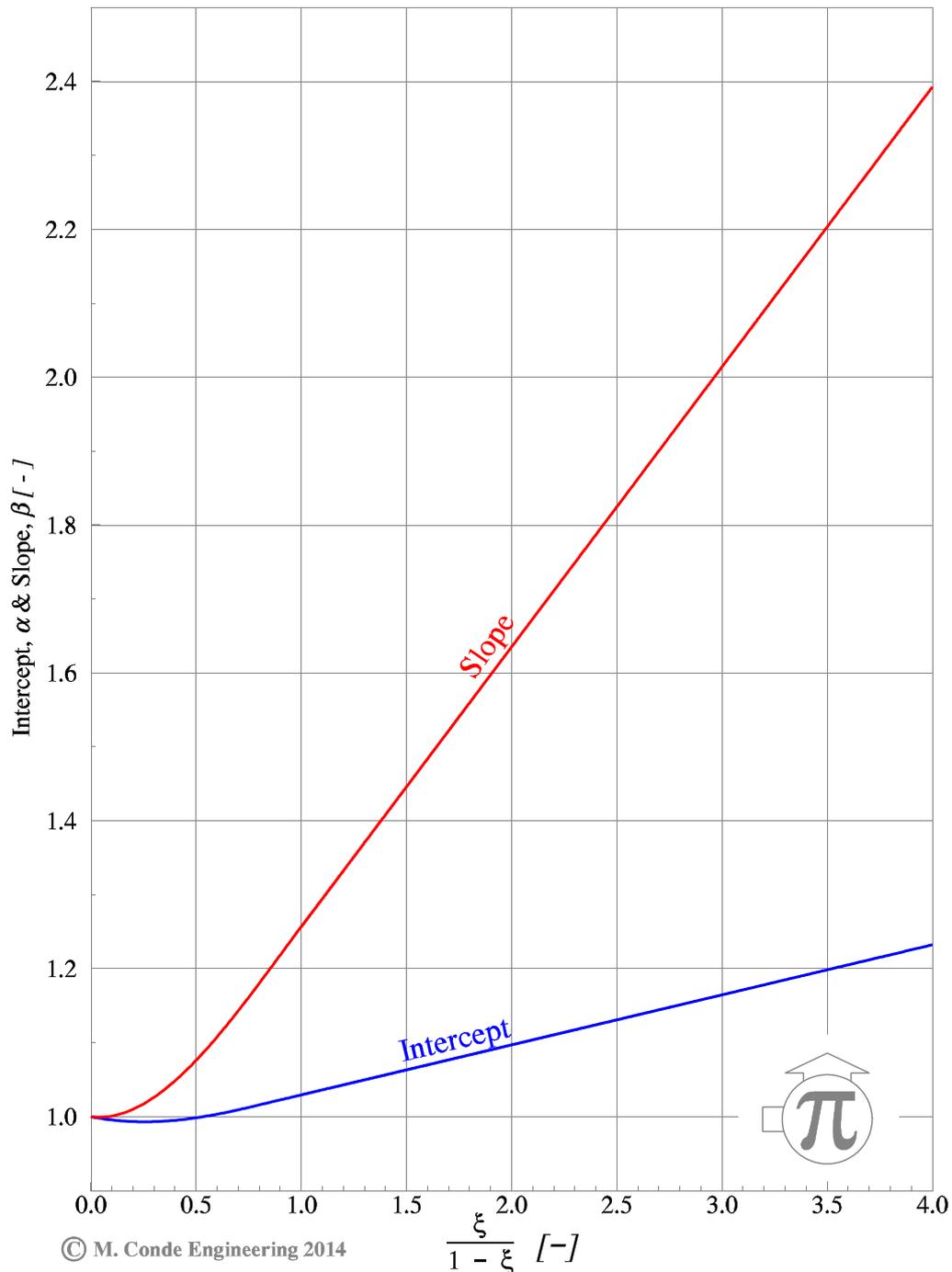
The straight lines obtained by this method are not parallel, resulting in intercepts  $a$  and slopes  $b$  that are function of the solute mass fraction. The  $c_i$  coefficients are given by Hoffmann and Florin for vapour pressures in *mmHg*, as

$c_1$	$c_2$	$c_3$	$c_4$
1.0	$-7.9151 \times 10^{-3}$	$2.6726 \times 10^{-3}$	$-0.8625 \times 10^{-6}$

The intercepts  $a$  and slopes  $b$  at constant solute mass fraction were determined from observed data in the literature<sup>14,16,18</sup>, and adimensionalized as

$$\alpha \equiv \frac{a}{a_{\xi=0.0}} \quad \beta \equiv \frac{b}{b_{\xi=0.0}} \quad (3)$$

$a$  and  $\beta$  were then plotted as depicted in Figure 2, and suitable functions sought that would represent both parameters adequately in the range of interest ( $0.0 \leq \xi \leq 0.8$ ).



**Figure 2** - Plot of the dimensionless intercept and slope of the Hoffmann and Florin vapour pressure equation for aqueous NaOH.

Both curves are characterized by two regions, a parabolic one for  $\xi \leq 0.50$ , and a straight line for  $0.5 \leq \xi \leq 0.80$ . A general equation, [4], applies to both curves with the parameters in Table 2.

$$\alpha = \begin{cases} a_4 \xi_r^5 + \sum_{i=0}^3 a_i \xi_r^i & \xi \leq 0.50 \\ a_5 + a_6 \xi_r & 0.5 < \xi \leq 0.80 \\ \xi_r = \frac{\xi}{1-\xi} & \end{cases} \quad (4)$$

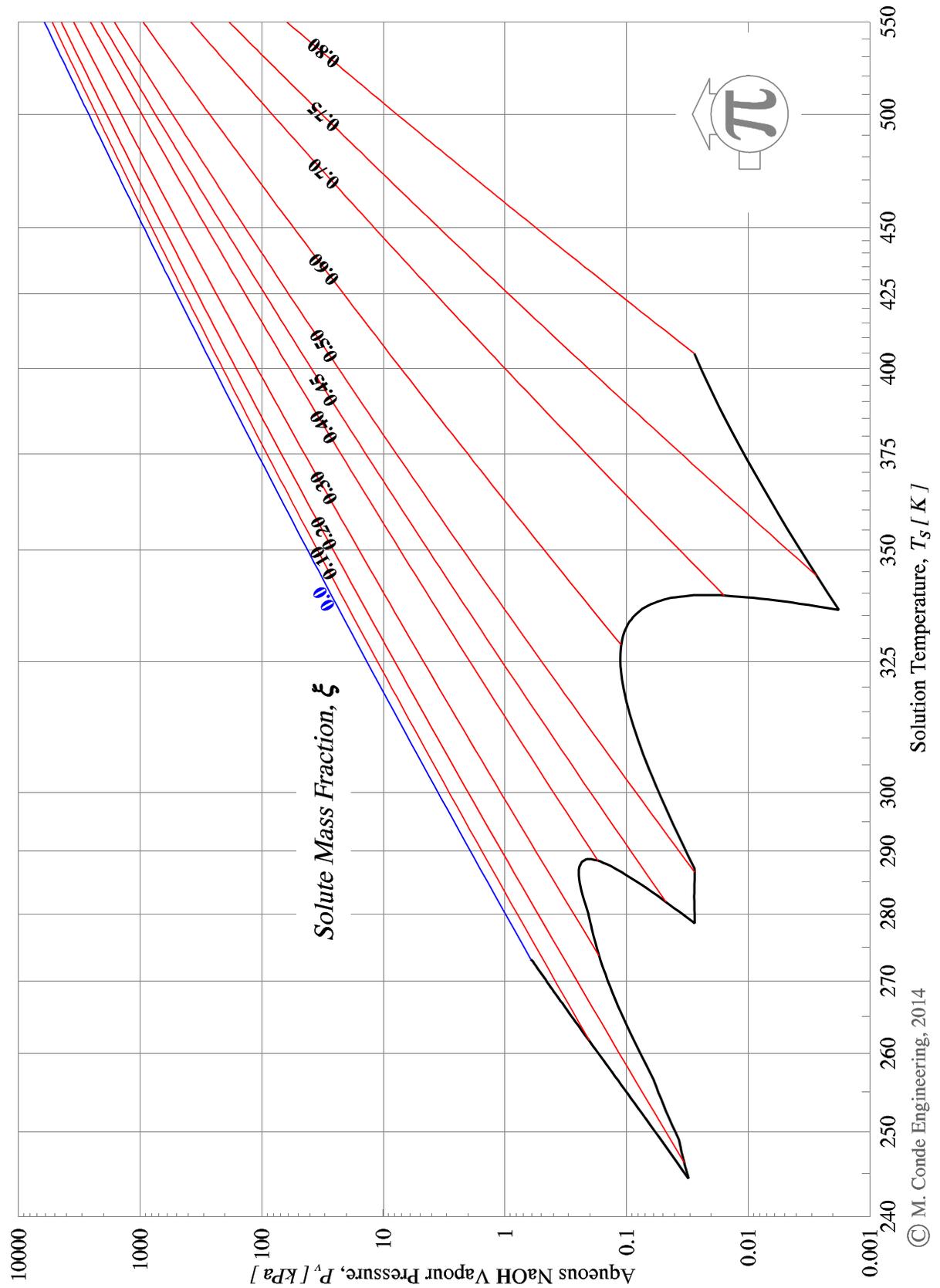
**Table 2** – Parameters of equations (4) to calculate the intercept  $\alpha$  and the slope  $\beta$  of isopleth lines.

	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$
Intercept, $a(\xi)$	1.0	-0.05639957	0.12222166	-0.02905165	-0.00735359	0.96182463	0.067636736
Slope, $\beta(\xi)$	1.0	0.03463341	0.45324069	-0.15759392	-0.00407556	0.926536441	0.399668179

The Intercept at  $\xi = 0.0$  is  $a_0 = 7.02344034$ , and the Slope at  $\xi = 0.0$  is  $\beta_0 = -3149.85631997$ . Finally, the vapour pressure  $P_v$  [kPa] is calculated as

$$P_v = 0.13332 \cdot 10^{\alpha_0 \cdot \alpha(\xi) + \frac{\beta_0 \cdot \beta(\xi)}{\tau(T)}} \quad (5)$$

An Othmer Chart created using the above described model is depicted in Figure 3 below. The values of  $a_0$  and  $\beta_0$  were maintained as for the vapour pressure of water in contact with the liquid phase, even for temperatures where pure water would have been solid. The rationale behind this was that vapour in contact with a liquid solution would behave similarly.



© M. Conde Engineering, 2014

**Figure 3 - An Othmer Diagram of aqueous NaOH.**

## References

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. Pickering, S. U. 1893. The hydrates of sodium, potassium and lithium hydroxides, *J. of the Chemical Society (London)*, 63, 890 - 909.
3. Braendl, F. 1962. Heterogene Gleichgewichte in Alkali-hydroxidschmelzen, Dissertation Universitaet Muenchen.
4. Cohen-Adad, R., A. Tranquard, R. Péronne, P. Negri, A.-P. Rollet, 1960. Le système eau-hydroxide de sodium, *Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences*, 251, 2035 - 2037.
5. Brodale, G. E., W. F. Giauque 1962. The freezing point - solubility curve of aqueous sodium hydroxide in the region near the anhydrous-monohydrate eutectic, *The Journal of Physical Chemistry*, 66, 2051.
6. Murch, L. E., W. F. Giauque 1962. The thermodynamic properties of sodium hydroxide and its monohydrate. Heat capacities to low temperatures. Heats of dilution, *The Journal of physical chemistry*, 66, 2052 - 2059.
7. Gmelins Handbuch der anorganischen Chemie, 1965. Natrium Ergaenzungsband, Lieferung 2, System.Nummer 21, 847-890, Verlag Chemie GmbH, Weinheim.
8. von Muralt, R. 1919. Ueber die Einwirkung von Natriumhydroxyd auf die  $\alpha$ -Naphthyamin-sulfosaeuren, Dissertation ETH Zurich.
9. Hayward, A. M., E. P. Perman 1931. Vapour pressure and heat of dilution. – Part VII. Vapour pressures of aqueous solutions of sodium hydroxide and alcoholic solutions of calcium chloride, *Trans. Faraday Society*, 27, 59-69.
10. Åkerloef, G., G. Kegeles 1940. Thermodynamics of concentrated aqueous solutions of sodium hydroxide, *J. American Chem. Soc.*, 62, 620-640.
11. Stokes, R. H. 1945. Isopiestic vapor pressure measurements of concentrated solutions of sodium hydroxide at 25 °C, *J. American Chem. Soc.*, 67, 1689-1691.
12. Stokes, R. H. 1947. The measurement of vapor pressures of aqueous solutions by bi-thermal equilibration through the vapor phase, *J. American Chem. Soc.*, 69, 1291-1296.
13. Kangro, W., A. Groenvelde 1962. Konzentrierte waeserige Loesungen, I., *Zeitschrift fuer Physikalische Chemie Neue Folge*, 32, 110-126.
14. Krey, J. 1970. Thermische und kalorische Zustandsgroessen des Systems Wasser-Natriumhydroxid, Dissertation, Universitaet Braunschweig.



15. Krey, J. 1972. Dampfdruck und Dichte des Systems  $H_2O-NaOH$ , Zeitschrift fuer Physikalische Chemie Neue Folge, 81, 252-273.
16. Campbell, A. N., O. N. Bhatnagar 1984. Osmotic and activity coefficients of sodium hydroxide in water from 150 to 250 °C, J. Chem. Eng. Data, 29, 166-168.
17. MacMullin, R. B. 1969. Algorithms for the vapor pressure of water over aqueous solutions of salt and caustic soda, J. Electrochem. Soc., 116(3), 416-419.
18. Balej, J. 1985. Water vapour partial pressures and water activities in potassium and sodium hydroxide solutions over wide concentration and temperature ranges, Int. J. Hydrogen Energy, 10(4), 233-243.
19. Peters, R., et al., 1996. A solvation model for vapor-liquid equilibria in the system  $H_2O-NaOH$  from 10 to 85 Wt%, Int. J. of Thermophysics, 17(1), 99-109.
20. Hoffmann, W., F. Florin 1943. Zweckmaessige Drastellung von Dampfdruckkurven, Z. VDI - Beiheft Verfahrenstechnik, 2.