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Solubility Behavior of Sodalite in High Ionic Strength Solutions at Elevated Temperatures: A Pitzer Model Description

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INTRODUCTION

- Sodalite ($Na_8[Al_6Si_6O_{24}][Cl, OH, I]_2 \bullet xH_2O$) is a candidate waste form for:
  - ^{129}I (half-life, 15.7 million years)
  - contaminated chloride-based electrolytes from electrorefinery of used nuclear fuel
- Lithium-substituted sodalite ($Li_2Na_6[Al_6Si_6O_{24}][Cl, OH, I]_2 \bullet xH_2O$) is a candidate waste form for the waste generated by the LiCl-Li_2O oxide reduction electrochemical process:
  - Electrolysis of Li_2O: $Li_2O \rightarrow 2Li^+ + O^{2-}$
  - Li^+ strips oxygen off of UO_2 or U_3O_8: $UO_x + 2xLi^+ \rightarrow U^0 + xLi_2O$
- Salt formations are the ideal medium for disposal of contaminated electrolytes from electrorefinery of used nuclear fuel and sodalite-based waste forms.
- Sodalite is also one of important minerals precipitating from the Bayer process in production of alumina.
- Accurate knowledge of solubilities of sodalite in a wide range of ionic strengths at elevated temperatures has important bearings on many fields including nuclear waste management.

PURPOSE OF THIS STUDY

- To retrieve solubility constants for the pure hydroxyl end member of sodalite, hydroxysodalite, (ideal formula, $Na_8[Al_6Si_6O_{24}][OH]_2 \bullet 3H_2O$), from the solubility data in a wide range of ionic strengths at elevated temperatures, by using the high temperature Al-Si Pitzer model (Xiong, 2013, 2014) that has been established.
- Modeling platform: EQ3/6 Version 8.0a

Xiong, Y.-L. (2013), American Mineralogist, 98:141-153.

Xiong, Y.-L. (2014), Chemical Geology, 373:37-49.

EXPERIMENTAL DATA USED

- Zeng and Li (2012) conducted systematic solubility studies of hydroxysodalite in high ionic strength solutions
- Experimental conditions: T = 30 ^oC, 45 ^oC, 60 ^oC, and 75 ^oC
- Starting material: Synthetic hydroxysodalite with well defined stoichiometry, $Na_{7.26}[Al_6Si_{6.12}O_{24}][OH]_{1.68}\bullet 2.91H_2O$
- Approaching equilibrium from undersaturation
- Supporting solutions:
  - 1.0 to 9.2 mol•kg^{-1} NaOH
- Wajima et al. (2007) determined the solution chemistry when hydroxysodalite was formed at 90 ^oC in NaOH solutions—used for validation test

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Wajima et al. (2007), American Mineralogist, 92:1105-1111.

Zeng and Li (2012), Ind. Eng. Chem. Res., 51:15192-15206.

High Temperature Al-Si Pitzer Model

(taken from Xiong, 2013, 2014)

Table 1. Equilibrium constants for silica and aluminum species considered in the Al-Si Pitzer model of Xiong (2013, 2014) up to 250 °C

Reaction	T, °C	log K	Reference
$H_4SiO_4 = H^+ + H_3SiO_4^-$	25	–9.68 ± 0.14	Fleming and Crerar, 1982
	50	–9.34 ± 0.16	Fleming and Crerar, 1982
	75	–9.10 ± 0.17	Fleming and Crerar, 1982
	100	–8.94 ± 0.16	Fleming and Crerar, 1982
$H_3SiO_4^- = H^+ + H_2SiO_4^{2-}$	25	–13.45 ± 0.07	Hershey and Millero, 1986
	50	–12.95 ± 0.25	Xiong, 2013
	75	–12.56 ± 0.25	Xiong, 2013
	100	–12.28 ± 0.25	Xiong, 2013
$2H_4SiO_4 = H^+ + H_5Si_2O_7^- + H_2O$	25	–8.50	Felmy et al., 2001
	50	–8.14 ± 0.25	Xiong, 2013
	75	–7.86 ± 0.25	Xiong, 2013
	100	–7.65 ± 0.25	Xiong, 2013
$H_5Si_2O_7^- = H^+ + H_4Si_2O_7^{2-}$	25	–10.90	Felmy et al., 2001
	50	–10.59 ± 0.25	Xiong, 2013
	75	–10.38 ± 0.25	Xiong, 2013
	100	–10.24 ± 0.25	Xiong, 2013
$3H_4SiO_4 = 3H^+ + H_5Si_3O_{10}^{3-} + 2H_2O$	25	–29.40	Felmy et al., 2001
	50	–28.75 ± 0.25	Xiong, 2013
	75	–28.34 ± 0.25	Xiong, 2013
	100	–28.11 ± 0.25	Xiong, 2013

High Temperature Al-Si Pitzer Model

(taken from Xiong, 2013, 2014)

Table 1. Equilibrium constants for silica and aluminum species considered in the Al-Si Pitzer model of Xiong (2013, 2014) up to 250 °C (Continued)

Reaction	T, ^{o}C	log K	Reference
$Al(OH)_4^- = Al^{3+} + 4OH^-$	25	–34.05 ± 0.05	Wesolowski, 1992
	50	–33.44 ± 0.05	Wesolowski, 1992
	75	–33.11 ± 0.05	Wesolowski, 1992
	100	–32.99 ± 0.05	Wesolowski, 1992
$AlOOH(cr) + 2H_2O = H^+ + Al(OH)_4^-$	100	–12.89 ± 0.04	Xiong, 2014
	150	–12.03 ± 0.05	Xiong, 2014
	200	–11.34 ± 0.05	Xiong, 2014
	250	–10.98 ± 0.06	Xiong, 2014
$Al(OH)_4^- + H_2SiO_4^{2-} = Al(OH)_3HSiO_4^{3-} + H_2O(l)$	20	–0.42 ± 0.10	Xiong, 2013
	25	–0.42 ± 0.15	Xiong, 2013
	50	–0.38 ± 0.25	Xiong, 2013
	75	–0.35 ± 0.25	Xiong, 2013
	100	–0.33 ± 0.25	Xiong, 2013

High Temperature Al-Si Pitzer Model

(taken from Xiong, 2013, 2014)

Table 2. Pitzer interaction parameters in the Al-Si Pitzer model of Xiong (2013, 2014) to 100^{o}C

Binary Interaction Parameters				
Interaction Pair	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	References
$Na^{+}–H_3SiO_4^{-}$	0.043±0.019	0.24±0.11		Hershey and Millero (1986)
$Na^{+}–H_2SiO_4^{2-}$	0.32±0.08	0.13±0.50		Hershey and Millero (1986)
$Na^{+}–H_5Si_2O_7^{-}$	–0.0571±0.04	0.34±0.13		Xiong (2013)
$Na^{+}–H_4Si_2O_7^{2-}$	–0.0227±0.06	1.56±0.40		Xiong (2013)
$Na^{+}–H_5Si_3O_{10}^{3-}$	0.078±0.03	4.29±0.80		Xiong (2013)
Na^{+}-$Al(OH)_3HSiO_4^{3-}$	0.078±0.03	4.29±0.80		Xiong (2013)
$Na^{+}–Al(OH)_4^{-}$	0.051	0.25	–0.00090	Wesolowski (1992)
Interaction Involving Neutral Species and Mixing Parameters				
Interaction Pair	λ_{ij}	θ_{ij}	Ψ_{ijk}	References
$Na^{+}–H_4SiO_4^{0}$	0.0925			Azaroual et al. (1997)
$OH^{-}–H_2SiO_4^{2-}$		–0.0812±0.003 $(\frac{\partial \theta_{ij}}{\partial T})_P =$ $-9.35\pm0.44\times10^{-5}$		Xiong (2013)
$OH^{-}–H_2SiO_4^{2-}–Na^{+}$			–0.017±0.02	Xiong (2013)
$OH^{-}–Al(OH)_4^{-}–Na^{+}$			–0.04800	Wesolowski (1992)
$Cl^{-}–Al(OH)_4^{-}–Na^{+}$			–0.04857	Xiong (2014)

Si Pitzer Model Validation Test (from Xiong, 2013)

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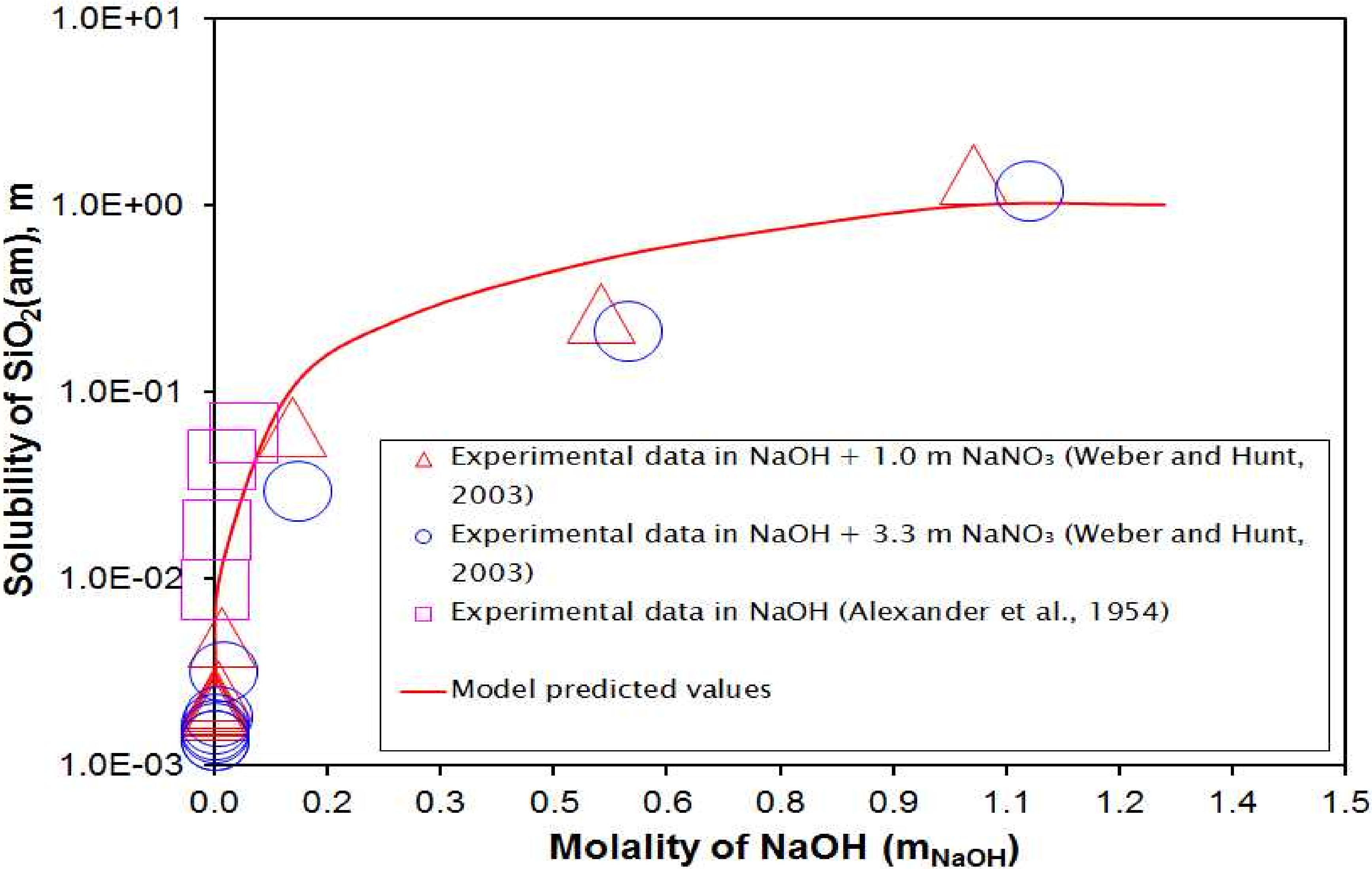
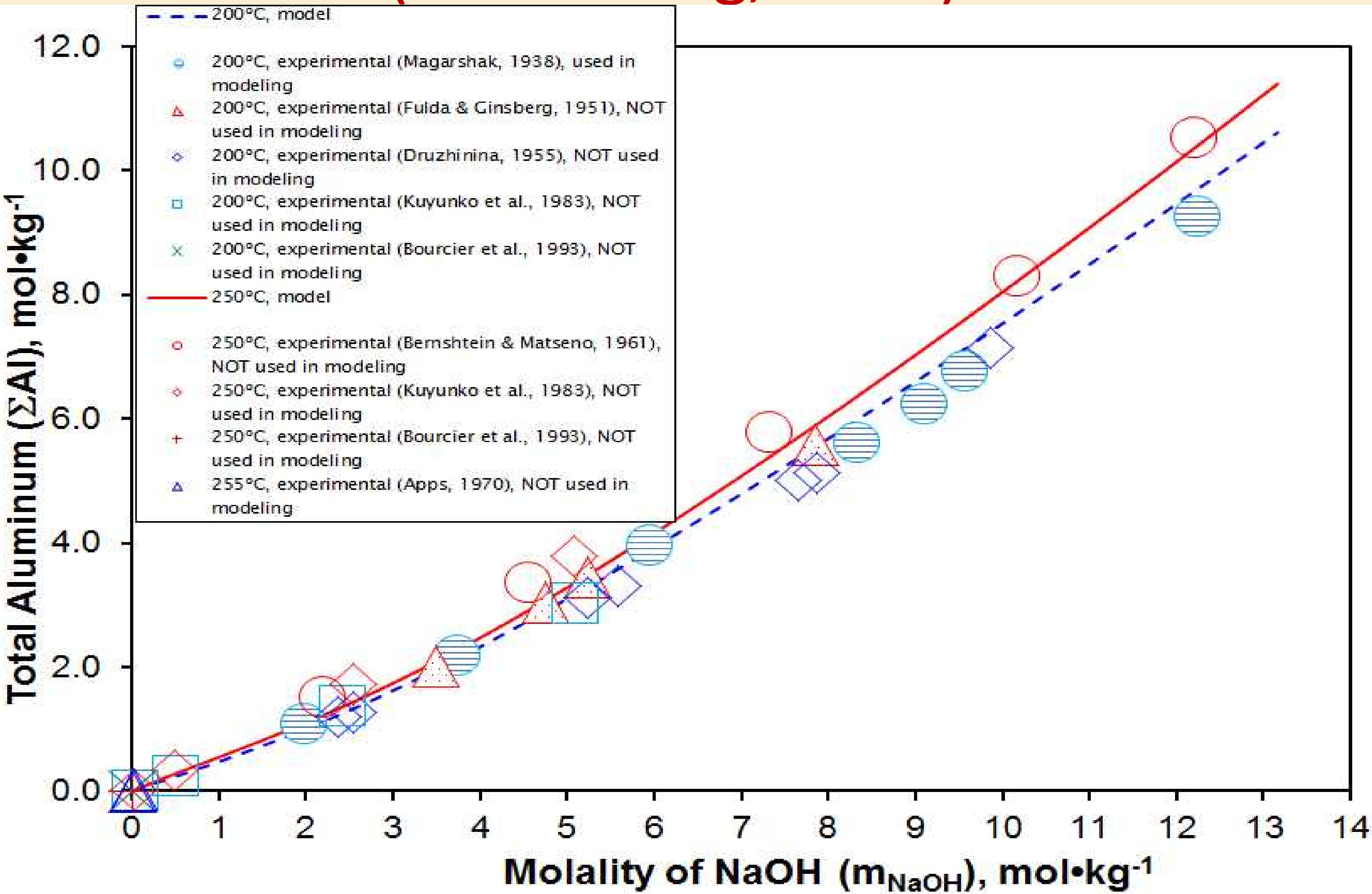


Al Pitzer Model Validation Test (from Xiong, 2014)

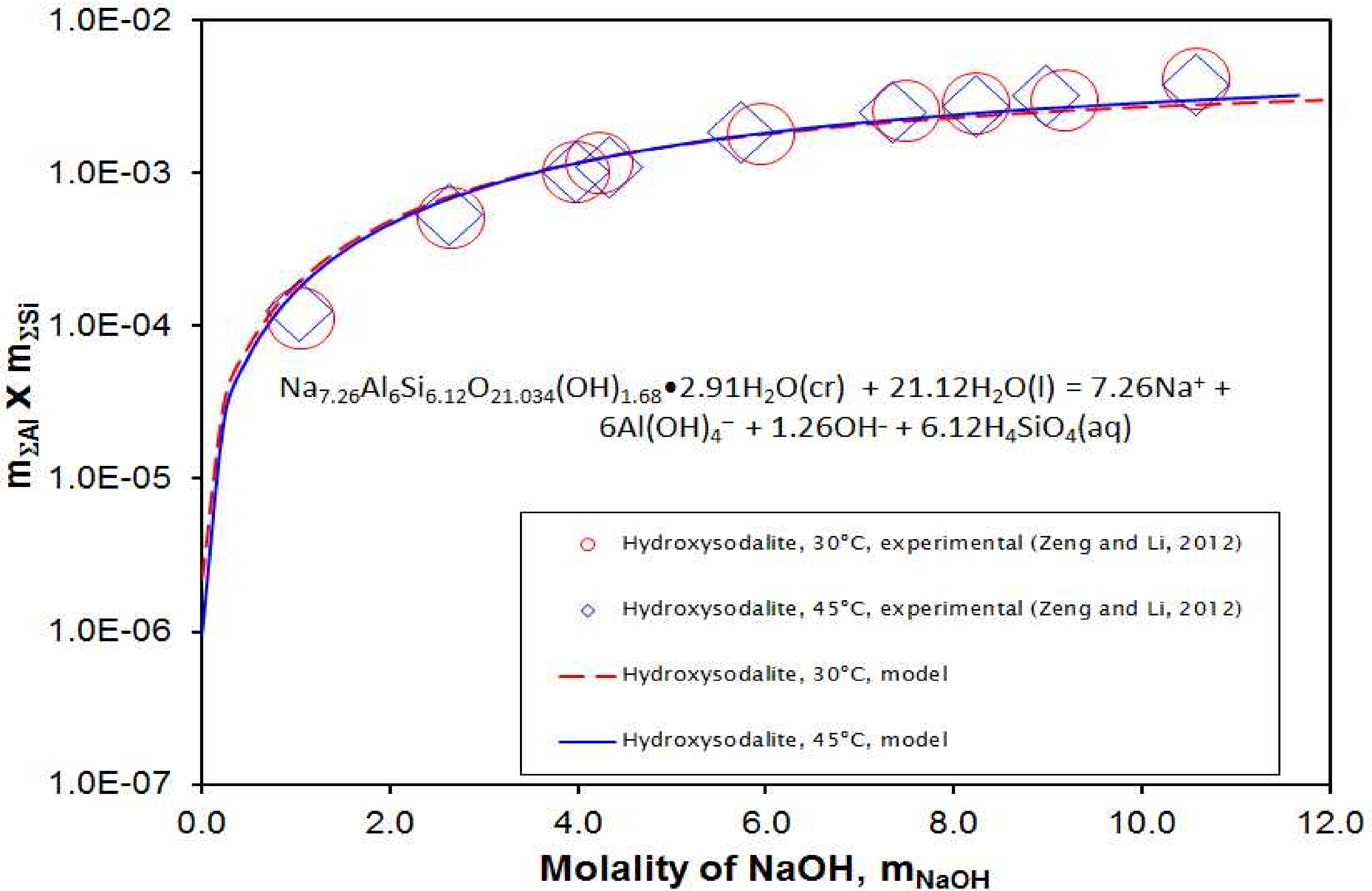


Hydroxysodalite: This Work

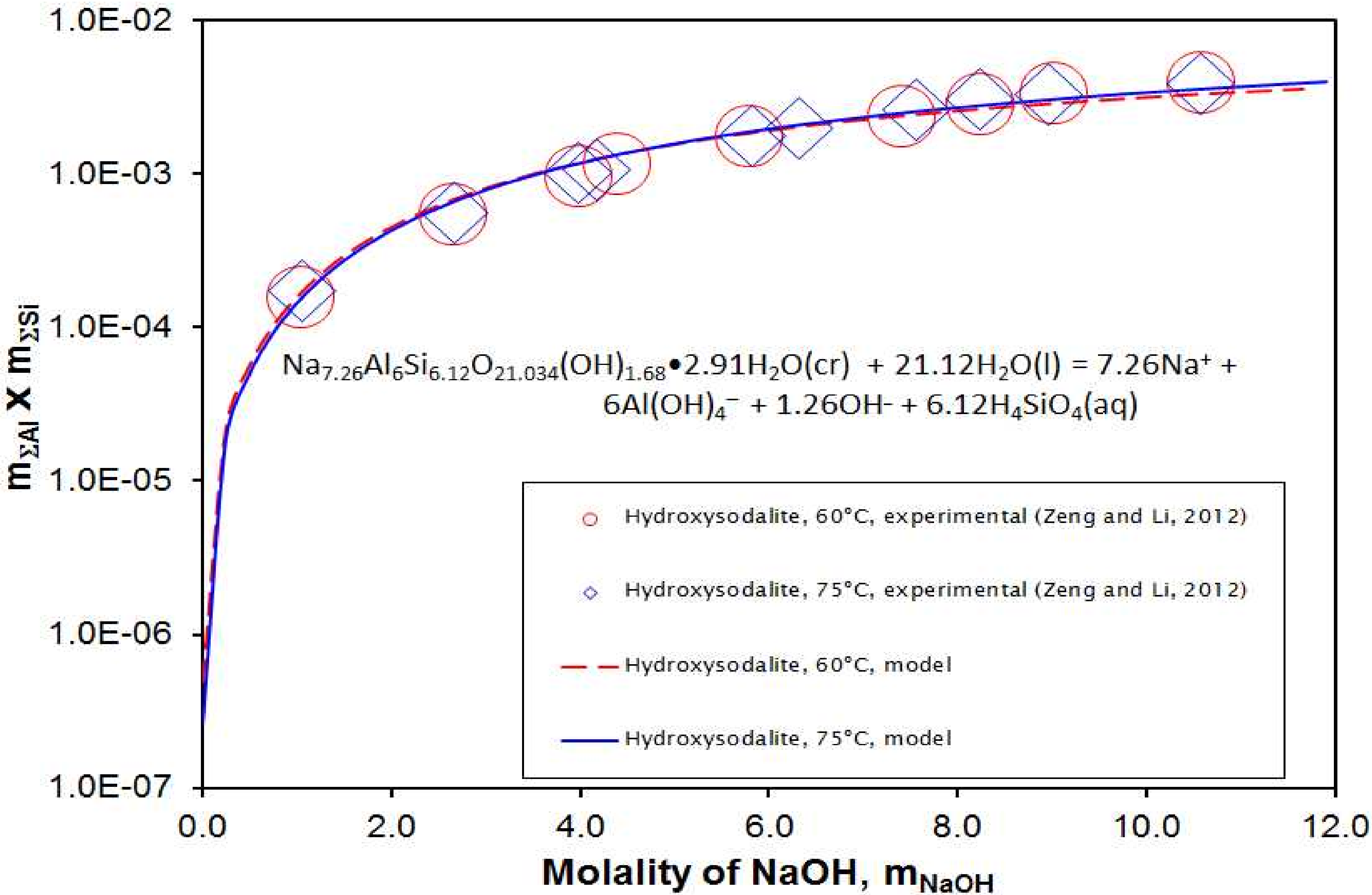
Solubility data from Zeng and Li (2012) are modeled for the solubility constants for the following reaction by applying the Al-Si Pitzer model:

$$Na_{7.26}Al_6Si_{6.12}O_{21.034}(OH)_{1.68}\bullet 2.91H_2O(cr) + 21.12H_2O(l)$$
$$= 7.26Na^+ + 6Al(OH)_4^- + 1.26OH^- + 6.12H_4SiO_4(aq)$$

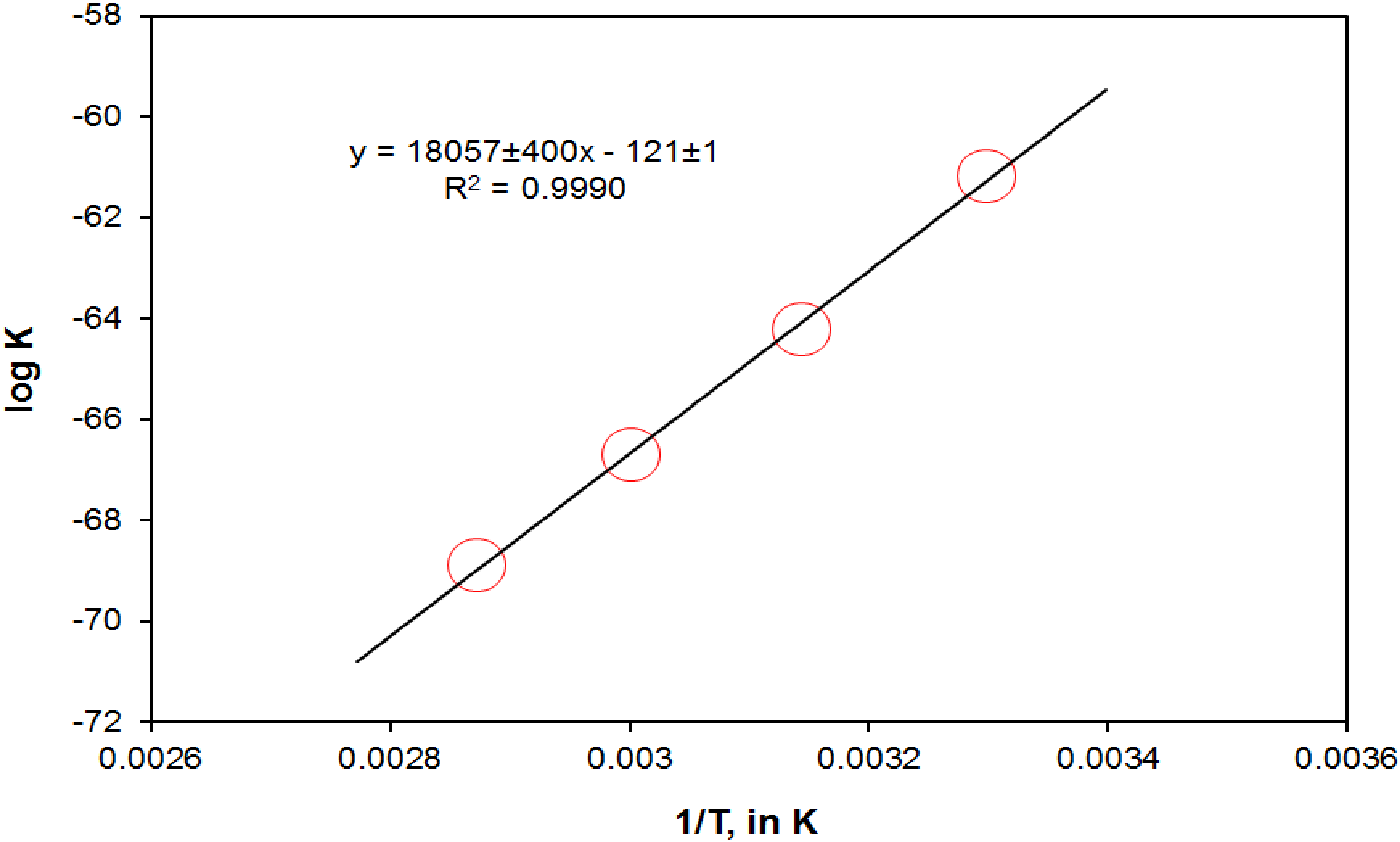
Hydroxysodalite



Hydroxysodalite



Hydroxysodalite: Temperature Function



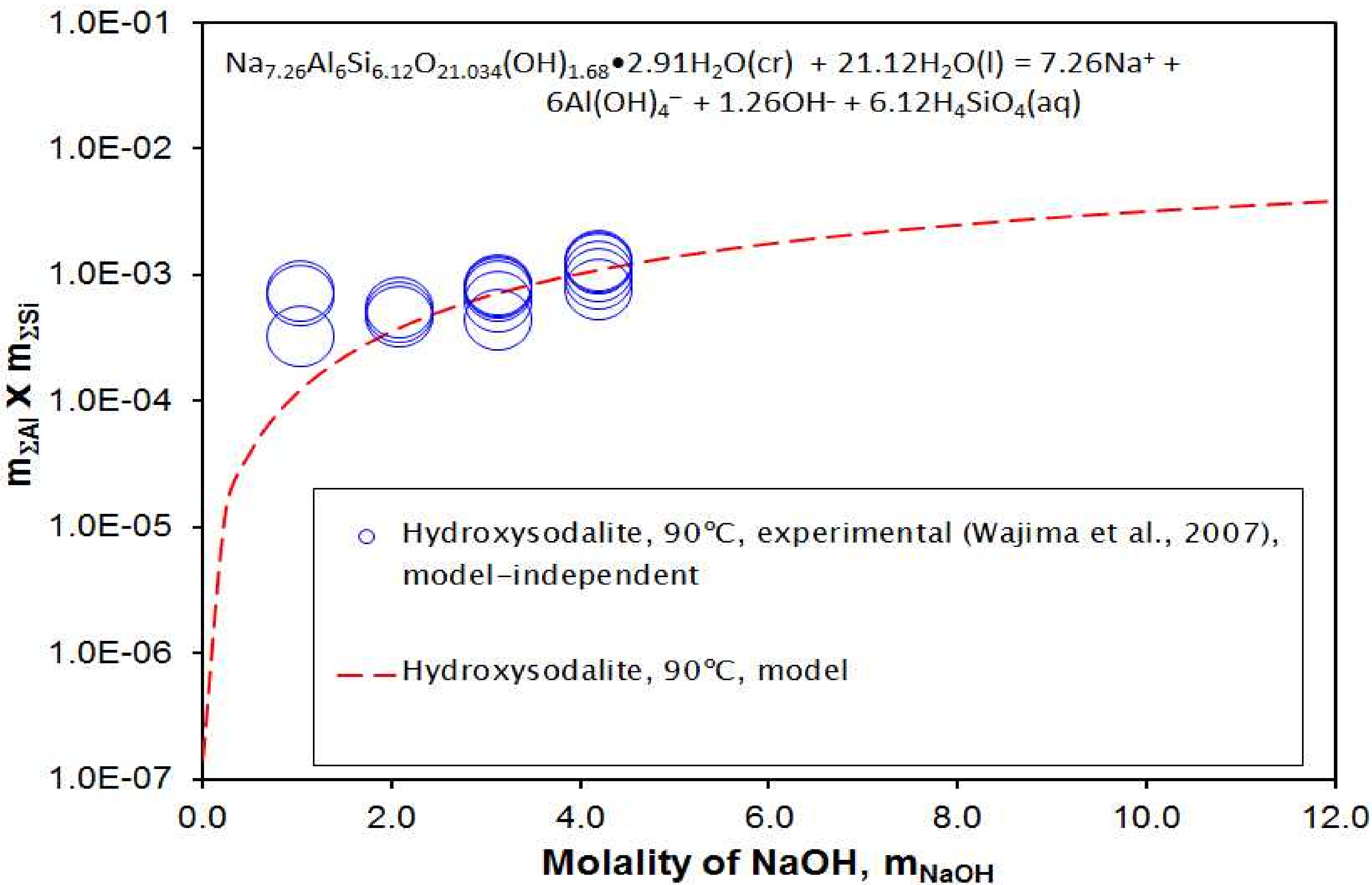
Hydroxysodalite: Temperature Function

Table 3. Equilibrium constants of hydroxysodalite retrieved from solubility experiments in this study

T, ^{o}C	log K	Reaction
25	–60.34 [A]	$Na_{7.26}Al_6Si_{6.21}O_{24.03}(OH)_{1.68}\cdot 2.91H_2O(cr) + 21.12H_2O(l) = 7.26Na^+ + 6Al(OH)_4^- + 1.26OH^- + 6.12H_4SiO_4(aq)$
30	–61.18	
45	–64.20	
60	–66.69	
75	–68.89	
90	–71.26 [A]	
100	–72.68 [A]	

[A] Extrapolated values, based on the linear relation between log *K* and reciprocal temperature in Kevin for hydroxysodalite.

Hydroxysodalite: Model Validation



Conclusions

In this study, an accurate thermodynamic model has been developed for describing solubility of hydroxysodalite at elevated temperatures to 100^{o}C and to high ionic strengths

- The model is validated by model-independent solubility data at 90^{o}C up to ionic strength of 4.2 mol•kg^{-1}.

References

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