



Solubility estimation of inorganic salts in supercritical water



F. Masoodiyeh^a, M.R. Mozdianfard^{a,*}, J. Karimi-Sabet^b

^a Department of Chemical Engineering, University of Kashan, Kashan, Iran

^b Jaber Ebne Hayyan National Research Laboratory, NSTRI, Tehran, Iran

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ABSTRACT

Presence of minute amount of inorganic salts in supercritical water (SCW) can cause equipment scaling, erosion and corrosion, reaction disturbance and process malfunctions. Thermodynamic modeling reduces experimental measurements; hence, solubility of several inorganic salts with available empirical solubility data (NaH_2PO_4 , Na_2HPO_4 , NaCl , CaCl_2 , MgCl_2 and MgSO_4) within temperature and pressure ranges of (623–823) K and (9.0–25.0) MPa, respectively, is estimated following determination of the dissociation constant, K , in SCW using three known models, namely, R-HKF, Sue–Adschiri–Arai (SAA) and Density model. Results obtained are compared with the experimental data to assess the suitability of the models in predicting the solubility of these inorganic salts in SCW, which indicate that R-HKF model is satisfactorily capable of correlating solubility for these salts. In almost every case except NaCl , SAA has provided similar estimation to R-HKF model. The Density model however, has offered the least accurate estimation in all cases.

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1. Introduction

Developments in the last two decades in environmental and energy efficient technologies has made super-critical water (SCW) one of the most promising solvents/environments for industrial applications such as hydrothermal conversion of biomass [1,2], destruction of waste sludge and organic waste compounds [3,4], particle formation on a micro/nano scale [5,6], reaction media for polymerizations and conversion processes [7,8], separation of inorganic compounds [9,10] and power plants [11,12]. SCW (critical temperature $T_c = 647$ K, critical pressure $P_c = 22.1$ MPa) varies to a large degree in its properties compared to the common phases of liquid and vapor [13]. Moreover, in SCW, properties like diffusion rate, density and viscosity are adjustable [14,15]. Often, in such industrial applications, minor concentrations of inorganic compounds are encountered in the feed stream [16,17]. However, water polarity is reduced in its super-critical state and with it the ability of water to dissolve inorganic compounds is decreased [18]. This leads to precipitation of dissolved salts into a solid phase, causing equipment damage due to erosion, scaling, and corrosion, or influencing the main reaction and processes inside the systems [19–21]. Therefore, different techniques including reactor modifications [22,23], separation before process and even fractionization of different salt fractions [24] are being considered to circumvent

salt formation. For the design of these new concepts and predict the influence of these compounds, and thereby, avoiding the associated problems faced in their presence, a profound knowledge of solubility of these inorganic compounds and their influence and behavior in SCW is required [25]. However, property data on systems containing SCW is scarcely available due to the extreme critical conditions of water; especially the degree of corrosion and mechanical stresses involved at such high temperatures and pressures, and also limited number of available industrial and commercial installations [13]. Therefore, solubility prediction of inorganic salts in SCW using appropriate models is necessary to link the results of the comparison (the quality of the fits) to the actual experimental data (solubilities of salts) to enhance the application of this promising technique.

In other application of SCW, namely, production of nanoparticles using hydrothermal synthesis, solubility prediction of inorganic compounds in SCW is also of utmost importance. In this regard, Hakuta *et al.* [26] evaluated the concentrations of aluminum species and studied the morphology of Boehmite particles (AlOOH) produced from a SCW hydrothermal method, accordingly. In another study carried out to investigate the influence of reactive phase behavior of $\text{Al}(\text{NO}_3)_3$, on various phases of Boehmite, at different temperatures and pressures, Wang *et al.* [27] presented speciation calculation using dissociation constants, K , of the synthesis reactions and the Density model (a model used in this study and defined in more detail in subsequent sections). Atashfaraz *et al.* [28] investigated the influence of TiO_2 solubility

* Corresponding author. Tel.: +98 3155912457; fax: +98 3155912444.

E-mail address: mozdianfard@kashanu.ac.ir (M.R. Mozdianfard).

Nomenclature

AAD	absolute average deviation	\bar{S}_{p_r, T_r}^0	standard molal entropy at the reference pressure and temperature ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
a_i	activity of the i th species	SAA	Sue–Adschiri–Arai
a_1, a_2, a_3, a_4	species specific revised-HKF equations of state regression parameters	SCW	super-critical water
c	designation of the critical condition	T	absolute temperature (K)
<i>calc</i>	designation of the calculated	T_r	reference temperature of 298.15 K
c_1, c_2	species-specific revised-HKF equations of state regression parameters	V_{p_r, T_r}^0	standard molal volume at the reference pressure and temperature ($\text{m}^3 \cdot \text{mol}^{-1}$)
\bar{C}_{p_r, T_r}^0	standard molal heat capacity at the reference pressure and temperature ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	w	designation of the water
<i>exp</i>	designation of the experimental	Y	Born function equal to $-5.8 \cdot 10^{-5} \text{K}^{-1}$ at the reference pressure and temperature
$\Delta G_{p, T}^0$	standard molal Gibbs free energy of formation from the elements in their stable form at $T = 298.15 \text{K}$ and 1 bar ($\text{J} \cdot \text{mol}^{-1}$)	z	charge of the ionic species
$\Delta G_{T, p_r}^0$	standard molal Gibbs free energy of reaction ($\text{J} \cdot \text{mol}^{-1}$)	<i>Greek letters</i>	
HKF	Helgeson–Kirkham–Flowers	α	coefficient of thermal expansion for H_2O
ΔH_r^0	standard molal enthalpy of formation from the elements in their stable form at $T = 298.15 \text{K}$ and 1 bar ($\text{J} \cdot \text{mol}^{-1}$)	ε	dielectric constant of water
I	ionic strength	ε_{p_r, T_r}	dielectric constant of water at the reference pressure and temperature
i, j	generic designation of a species	Θ	solvent parameter equal to $T = 228 \text{K}$ for water
K	dissociation constant	ρ	molar density ($\text{mol} \cdot \text{m}^{-3}$)
NP	number of data points	Ψ	solvent parameter equal to 2600 bar for water
P	pressure (bar)	γ_i	activity coefficient for the i th aqueous species
p_r	reference pressure of 1 bar	ν_{ij}	stoichiometric coefficient of species j in reaction i
R	gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	ω	Born solvation parameter ($\text{m}^3 \cdot \text{mol}^{-1}$)
RMSD	root-mean-square deviation	ω_{p_r, T_r}	Born solvation at the subscripted reference pressure and temperature ($\text{m}^3 \cdot \text{mol}^{-1}$)
r	designation of the reference		

at various pH's in SCW hydrothermal synthesis of BaTiO_3 nanoparticles, considering chemical dissociation constants calculated also from the Density model, thereby determining the suitable pH for the synthesis.

In this study, the solubility of several common inorganic salts with available empirical solubility data such as NaH_2PO_4 , Na_2HPO_4 , NaCl , CaCl_2 , MgCl_2 and MgSO_4 is estimated following determination of K , or the dissociation constant in SCW using several appropriate known models as selected below. To obtain K of a reaction however, the standard molal Gibbs free energy of formation of the reaction products and reactants is required. When dealing with aqueous compounds, Criss–Cobble method is used in evaluating temperature-dependent thermodynamic properties [29,30]. This method however, can only be applied to temperatures below 473 K and there are limited parameters available for it in case of certain types of complex species. To overcome this, Helgeson–Kirkham–Flowers (HKF) [31] and later the revised HKF (R-HKF) models were proposed [32–34] which were capable of evaluating standard partial thermodynamic properties of any aqueous species at higher temperatures and pressures. In R-HKF model however, standard molal Gibbs free energy of formation, $\Delta G_{T, p_r}^0$, standard molal entropy, S_{T, p_r}^0 , standard molal heat capacity, C_{p_r, T_r}^0 , standard molal volume, V_{T, p_r}^0 , and Born solvation, ω_{T, p_r}^0 (all of them at reference temperature and pressure) for each species are required. Shock *et al.* [34] provided a database for these parameters. For inorganic salts, the number of experimentally determined V_{T, p_r}^0 data are less available. Hence, Sue *et al.* [35] presented a model (SAA) where they eliminated the parameter needed for V_{T, p_r}^0 , by simplifying the empirical part of R-HKF model to be expressed in terms of temperature and water density, instead of temperature and pressure. Temperature and density had already been used in a simple empirical model [36] for data correlation, where later Anderson *et al.* [37]

gave physical meaning to constants related to terms containing these, following performing a thermodynamic analysis. Several studies have adopted this so called 'Density model' for predicting K at higher temperatures and pressures [26,28,38].

In this study of solubility estimation for inorganic salts at high temperatures and pressures, three of the above thermodynamic models, namely, R-HKF, SAA and Density model have been used to calculate K and compare the results with the experimental data available in the literature, thereby assessing the suitability of the models in predicting the solubility of these common inorganic salts in SCW.

2. Theory and modeling

2.1. Dissociation constant

As explained above, the dissociation constant K , is evaluated in this study using three models of R-HKF [32], Density model [37] and SAA [35], over a wide range of temperatures and pressures including the critical point. These are introduced briefly here with more detailed explanations given in Appendix A1, where purposes for which these models are development are also expressed.

2.1.1. R-HKF model

The HKF model [31] has been successfully applied to the correlation of the equilibrium constant for hundreds of inorganic aqueous species of interest to geochemistry over a wide range of conditions ($T = (298 \text{ to } 1273) \text{K}$ and $(1 \text{ to } 5000) \text{bar}$). In this model, the standard partial molal Gibbs free energy of formation, ΔG_i^0 , at given temperatures and pressures is described by the following relation:

$$\Delta G_i^0 = \Delta G_{r,i}^0 + \Delta G_{s,i}^0 + \Delta G_{n,i}^0 \quad (1)$$

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