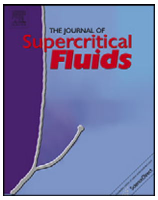
J. of Supercritical Fluids 50 (2009) 1–5

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu



Effect of cation species on solubilities of metal chlorides in water vapor at high temperatures and pressures

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ARTICLE INFO

Article history:
Received 22 January 2009
Received in revised form 8 April 2009
Accepted 8 April 2009

Keywords:
Water vapor
Solubility
Metal chloride

ABSTRACT

A flow type apparatus was used for the measurements of the solubilities of lithium chloride and calcium chloride in water vapor from 623 to 673 K and from 6.0 to 14.0 MPa. The solubilities of both metal chlorides increase with temperatures at the constant pressure. This behavior implies that the systems form the vapor–liquid equilibria at the conditions focused in this work unlike the case of sodium chloride and potassium chloride reported previously. A correlation model was developed for the solubilities of the metal chlorides in water vapor. The ionizations and hydrations of the metal chlorides were considered in the correlation model. The solubility data for the sodium chloride, potassium chloride, lithium chloride and calcium chloride in water vapor were correlated. The correlated results are in good agreement with the experimental data. The hydration numbers of metal chlorides were obtained from the correlations. It was found that the hydration numbers for the metal chlorides with monovalent cations increase with the radii of cations. For calcium chloride, the value of the hydration number is larger than those for metal chlorides with monovalent cations.

1. Introduction

Supercritical water oxidation (SCWO) technologies have been applied to decompose the toxic organics [1,2], such as dioxin and poly-chloro-biphenyl (PCB), to CO_2 and H_2O. In these processes, hydrogen halides such as hydrochloric acid are produced and cause remarkable corrosion of reactor. Alkalis are added as the neutralization reagent in order to prevent the corrosion and metal chlorides are produced. These metal chlorides in supercritical water are precipitated in the reactor or lines because of the very low solubilities of the metal chlorides in supercritical water. The effective discharges of the metal chlorides from the system are required. Therefore, it is important for the development of the supercritical water oxidation processes to understand the solubilities of metal chlorides in supercritical water and the phase behavior for supercritical water + metal chloride systems.

The solubilities of sodium chloride in water vapor at high temperatures and pressures have been reported by some research groups [3–6]. Bischoff et al. [3] measured the solubilities of sodium chloride in sub- and supercritical water at the vapor–liquid equilibrium regions by a static method. On the other hand, the solubilities of sodium chloride in supercritical water were determined from a dynamic method by Armellini and Tester [5]. For water + potassium chloride system, the vapor–liquid equilibria at 653.2 and 683.2 K were measured by Hovey et al. [7]. The vapor–liquid equilibria for water + calcium chloride system at 653–773 K were also measured by Bischoff et al. [8]. Higashi et al. [9] have reported the solubilities of sodium and potassium chlorides in water vapor at 623–673 K at solid–vapor equilibrium regions. It has been described that the solubilities of sodium chloride are similar to those of potassium chloride at these temperature conditions. The empirical equations of state for water + sodium chloride and water + potassium chloride systems have been proposed by Pitzer and co-workers [7,10,11]. Shin et al. [12] have applied a solution model for the correlation of the solubilities of inorganic salts in supercritical water. The correlated results by the solution model represent the experimental data well. Higashi et al. [13] have also reported the correlations of solubilities of alkali metal chlorides in water vapor using association model.

The knowledge about the effects of the cation species for metal chlorides on the solubilities in water vapor at high temperatures and pressures is highly useful to select the alkalis for the neutralization of the hydrogen halides in the SCWO processes. The solubilities of metal chlorides in water vapor and phase behavior for water + metal chloride systems near the critical temperature of water are also required to prevent the precipitations of metal chlorides in the line from the reactor to the separator, especially. In this work, the solubilities of lithium chloride and calcium chloride in water vapor were measured from 623 to 673 K and from 6.0 to

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doi:10.1016/j.supflu.2009.04.007

14.0 MPa by a flow method. The solubility data of sodium chloride, potassium chloride, lithium chloride and calcium chloride were correlated by a correlation model developed in this work.

2. Experimental

2.1. Materials

Special grade of lithium chloride and calcium chloride were supplied from Wako Pure Chemical Industries Ltd. The purities of lithium chloride and calcium chloride were more than 95.0 and 99.0%, respectively. These chemicals were used without further purification. Ultra pure water obtained by deionization using MILLIQ LABO (Millipore Corporation) was used.

2.2. Apparatus and procedure

A flow type apparatus was used for the measurements of the solubilities for lithium chloride and calcium chloride in water vapor at high temperatures and pressures. The experimental apparatus and procedure were quite similar to those in a previous work [9]. The detailed descriptions of the apparatus and operating procedures were given in the previous work. The apparatus and procedures are only briefly described here. An equilibrium cell was made of Hastelloy C. The inside diameter and volume were about 12 mm and 10 ml, respectively. The cell was set in an air bath in which the temperatures were controlled within ±0.5 K. In the equilibrium cell, 2 g of lithium chloride or calcium chloride was introduced beforehand with the solubility measurements. This initial mass of metal chloride was larger than those in the case of NaCl and KCl in the previous work [9]. The equilibrium cell in the air bath was heated up to the desired temperatures. Pure water was supplied by a feed pump. A back pressure regulator was used for the control of the pressures in the system. The pressures in the system were maintained within ±0.05 MPa. The pressurized water was heated through a preheating coil and supplied to the equilibrium cell. At the outlet of the cell, pure water was also supplied to the outlet of the cell in order to avoid the precipitations of metal chlorides. Water vapor passed through the cell was decompressed at an expansion valve. The trapped samples were analyzed by ion chromatography (JASCO Co., Ltd.). The cation concentrations were obtained from the analysis. The solubilities of metal chlorides in water vapor were determined from the cation concentrations of metal chlorides and the flow rates of water measured at the sampling unit. The samplings were performed for 150 min. The compositions of metal chloride were checked every 30 min. The solubilities were determined from using the data of the sampling time in which the compositions were stable. The flow rates of water were 2.0–4.0 g min^{-1} which did not affect the results of the solubilities.

2.3. Results and discussion

The experimental results of the solubilities for lithium chloride and calcium chloride in water vapor are shown in Table 1 and Fig. 1. For both the metal chlorides, the solubilities in water vapor at focused conditions in this work increased with pressure. The solubilities of lithium chloride and calcium chloride are compared with those of sodium chloride and potassium chloride obtained in our previous work [9] as shown in Fig. 2. The solubilities increase with temperature for lithium chloride and calcium chloride, unlike sodium chloride and potassium chloride. It is thought that this behavior is caused from the differences of the phase state, vapor–liquid equilibria for lithium chloride and calcium chloride and solid–vapor equilibria for sodium chloride and potassium chloride. A measurement using the large amounts of the metal chloride in the equilibrium cell was carried out in order to check the phase

Table 1
Experimental result of solubilities for metal chloride (2) in water vapor (1).

T (K)	p (MPa)	$(w_2 \pm \sigma) \times 10^6$ [a]
LiCl		
623	7.0	5.1 ± 0.6
	8.0	8.0 ± 0.3
	9.0	9.9 ± 0.4
	10.0	11.4 ± 0.4
	11.0	13.1 ± 0.8
643	7.0	6.5 ± 0.5
	8.0	10.2 ± 0.2
	9.0	12.8 ± 0.6
	10.0	14.9 ± 0.3
	11.0	17.6 ± 0.7
653	8.0	11.6 ± 0.4
	9.0	16.4 ± 0.7
	10.0	25.4 ± 0.5
	11.0	31.5 ± 0.5
673	6.0	6.1 ± 0.1
	7.0	8.7 ± 0.4
	8.0	12.3 ± 0.3
	9.0	18.1 ± 0.7
	10.0	28.4 ± 0.7
	11.0	44.2 ± 0.7
$CaCl_2$		
623	11.0	0.41 ± 0.07
	12.0	0.66 ± 0.02
	13.0	1.6 ± 0.2
	14.0	3.3 ± 0.2
673	11.0	0.54 ± 0.03
	12.0	1.2 ± 0.1
	13.0	4.9 ± 0.4
	14.0	8.0 ± 0.5

[a] Repeatability of experimental data σ is defined in following equation. $\sigma = \frac{1}{N}\sum_{i=1}^{N}\left|w_2 - w_2^{(i)}\right|$, N: number of data points.

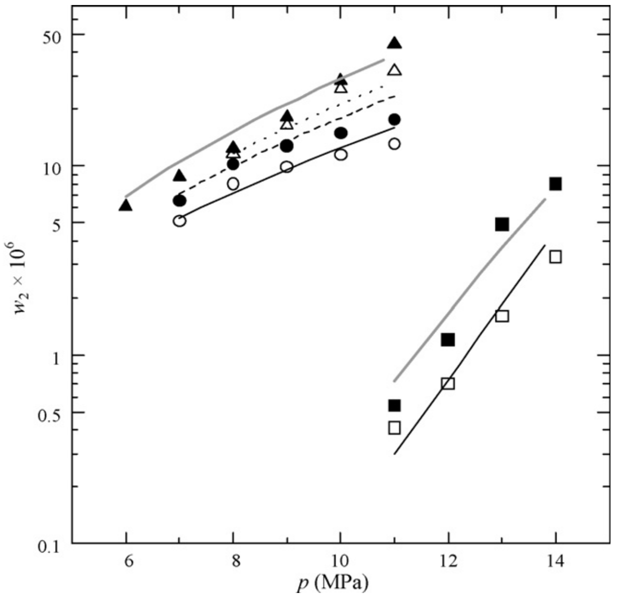

Fig. 1. Solubilities for lithium chloride and calcium chloride in water vapor. Experimental: LiCl (○) 623 K, (●) 643 K, (△) 653 K and (▲) 673 K. $CaCl_2$ (□) 623 K and (■) 673 K. Calculated: (——) 623 K, (- - - - -) 643 K, (.........) 653 K and (▬▬) 673 K.