Vestnik Otdelenia nauk o Zemle RAN, VOL. 3, NZ6099, doi:10.2205/2011NZ000229, 2011

Experimental study of the ZrO_2 solubility in water solutions of perchloric acid at 150°C

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Key words: zirconium dioxide, solubility, aqueous solutions, hydroxide complexes

Citation: Shikina, N. D., O. N. Medvedkina, E. S. Popova, R. B. Tagirov, Yu. K. Shazzo, I. L. Khodakovsky (2011), Experimental study of the ZrO_2 solubility in water solutions of perchloric acid at 150°C, *Vestn. Otd. nauk Zemle, 3*, NZ6099, doi:10.2205/2011NZ000229.

Zirconium is widely used in nuclear technologies. Because it is important to know conditions determining its behavior in water solutions not only for the physicochemical analysis of natural systems containing zirconium minerals, but also for many technological systems, in particular, studied to reach a compromise between the radioactive wastes disposals.

Literature data on solubility of Zr oxide and hydroxides of various degree of "aging" in water and water solutions at 25°C are listed in table 1.

Table 1. Solubility of the Zr oxide and hydroxides in water and water solutions at 25°C presented in the literature

Author	Phase	The time of achievement of equilibrium	pH-range	The Zr concentration
[*Bilinski and Branica*, 1966]	$Zr(OH)_4$ (amorphous)	24 hours	0–10	$n\cdot10^{-4}$ M
[*Samchuk and Dorofey*, 1983]	γ-$ZrO(OH)_2\cdot H_2O$	a month	7.17	$4.0\cdot10^{-7}$m
[Veyland, 1999]	γ-$ZrO(OH)_2\cdot H_2O$?		1.3 N	from $(4\div8)\cdot10^{-3}$m
[*Curti and Degueldre*, 2002]	ZrO_2(monoclinic) ZrO_2(cubic)	250 days	~7	$(5.5\pm0.6)\cdot10^{-9}$M $(6.9\pm0.6)\cdot10^{-9}$M
[*Ekberg, et al.*, 2004]	$Zr(OH)_4$ (Aldrich, 97%)	3 days	0-15	$\sim10^{-8}$M
[*Sasaki, et al.*, 2006]	$ZrO_2\cdot xH_2O$	6 month	1-4 5-13	0,001M $<10^{-8}$M
[*Altmaier, et al.*, 2008]	$ZrO_2\cdot xH_2O$	a month	1-3 3-10 11-14	0,001-10^{-8}M 10^{-8}M 10^{-8}-10^{-5}M
[*Qiu, et al.*, 2009]	ZrO_2	several hundreds of hours	4-11	$0.9-12\cdot10^{-8}$ mol/kg

As will be apparent from the table 1, neutral polynuclear particles $Zr_4(OH)_{16}^{o}(aq)$ rather quickly collapse (for a month the solubility decreases almost for three orders of magnitude). However, at low temperatures their concentrations can essentially exceed the concentrations of the monomeric complexes, $Zr(OH)_4^{o}(aq)$. A rise in temperature should increase not only the speeds of $ZrO_2(cr)$ dissolution reactions but also the speed of the reactions of the polynuclear particles depolymerization.

In the work [*Curti and Degueldre*, 2002] measured solubilities of ZrO_2(monoclinic) and ZrO_2(cubic) in the deionized water and $NaHCO_3$ water solutions ($5\cdot10^{-3}$; $5\cdot10^{-2}$ и $5\cdot10^{-1}$ M $NaHCO_3$) are presented. Samples of a solution (5 ml) were taken after 1, 12, 43 and 250 days. Zr concentration was measured using ICP-MS method.

The detailed analysis of the data shows the interesting aspects connected with kinetics of the dissolution reaction. The schedules specify in almost identical final concentration of zirconium in the solutions which are in equilibrium with the metastable cubic form and with stable monoclinic form of the zirconium's dioxide. The highest content of zirconium in water has been defined in the experiments with duration of 42-43 days.

The kinetics changes of the Zr concentration for ZrO_2(monoclinic) and ZrO_2(cubic) in water and $NaHCO_3$ solutions is shown In figure 1.

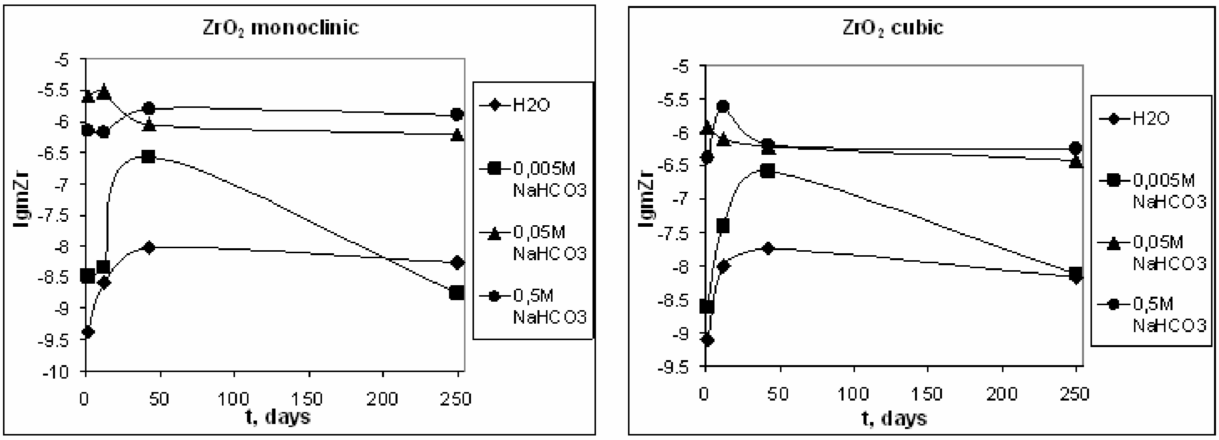

Fig. 1. Dependence of the ZrO_2(monoclinic) and ZrO_2(cubic) solubility on time [*Curti and Degueldre*, 2002]

The results of the experiments show the ZrO_2 solubility in the deionized water and in 0.005 M $NaHCO_3$ at duration of experiments of 250 days was not affected by the presence of a sodium hydrocarbonate in the system and, thus, they may be used, for calculation of an equilibrium constant of reaction: $ZrO_2(cr) + 2H_2O(l) = Zr(OH)_4°(aq)$, so this data may be averaged. Then we receive $lgmZr(OH)_4°(aq) = -8.5\pm0.25$ for ZrO_2(monoclinic) and $lgmZr(OH)_4°(aq) = -8.14\pm0.1$ for ZrO_2(cubic). These values will be consistent with the metastability of ZrO_2(cubic) in relation to ZrO_2(monoclinic) at 25°C.

As the data on hydrolysis of the Zr^{4+} ions, presented in the reference book [*Brown, etc.*, 2005], isn't complete, we performed new experimental studies of the ZrO_2-H_2O system with well characterized sample of the ZrO_2 monocrystals.

We used as an investigated the baddeleyite (ZrO_2) from Kovdor, kindly put at our disposal by B.N. Ryzhenko and N.I. Kovalenko. Experiments were performed in autoclaves from BT-8 titanic alloy with teflon bushes of volume ~ 30 ml. A solid phase was placed in the bush in teflon cups on legs so that contact of a solid phase to a solution surfaces occurred at lifting of the solution surfaces at heating. Teflon limings were used for hermetically sealing.

Zr concentration in the solutions was determined using a method of mass spectrometry with inductively connected plasma on the device X Series 2.

The results of our measurements of the ZrO_2(cr) solubility at 150°C and pressure of saturated steam are presented in table 2 and in figure 2.

The received results of solubility ZrO_2(cr) at 150°C and saturated steam pressure have been used for calculation of thermodynamic constants of equilibrium of reactions:

$ZrO_2(cr) + 2H_2O(l) = Zr(OH)_4°(aq)$ $\qquad lgK°_1 = -8.84\pm0.23$ (1)

$ZrO_2(cr) + H_2O(l) + H^+ = Zr(OH)_3^+(aq)$ $\qquad lgK°_2 = -7.61\pm0.10$ (2)

$Zr(OH)_3^+ + H_2O(l) = Zr(OH)_4°(aq) + H^+$ $\qquad lgK°_3 = -1.23\pm0.25$ (3)

Comparison of the received results with the literary data on solubility of ZrO_2(cr) in water, and also in solutions $NaHCO_3$ and LiOH (pict. 3) is spent.

Temperature dependence of an equilibrium constant of reaction (1) is found:

$lgK° = 2950/T + 17.4\cdot lgT – 61.5$ (4)

Table 2. Solubility of ZrO_2 in water solutions of perchloric acid at 150°C

$mHClO_4$	The number of experiments	ZrO_2 solubility mol/kg H_2O, 10^{-8}
0.001	3	0.20±0.06
0.01	4	0.12±0.05
0.05	6	0.21±0.05
0.1	5	0.44±0.07
0.251	1	0.88
0.5	2	4.3±2.0

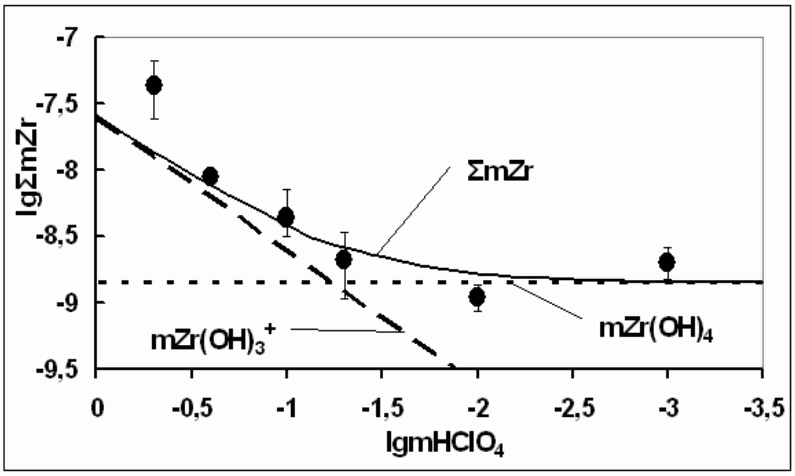

Fig. 2. Solubility of ZrO_2 in water solutions of perchloric acid at 150°C

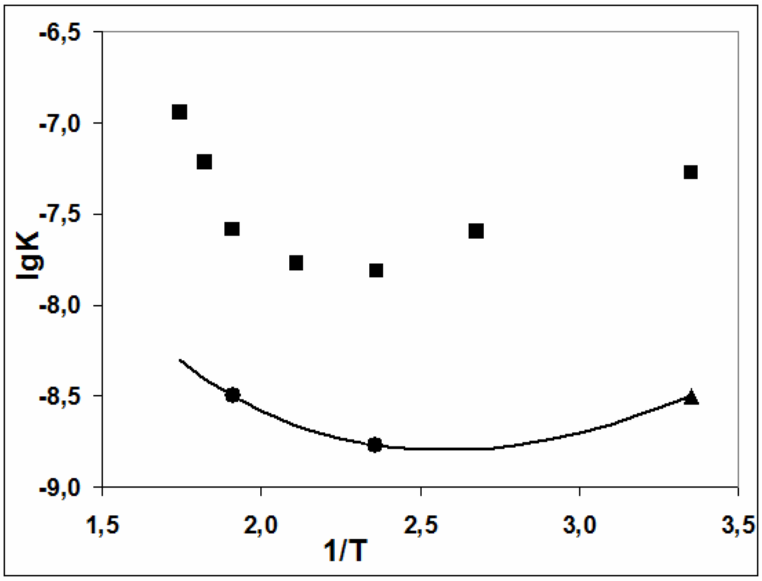

Fig. 3. Temperature dependence of an equilibrium constant of reaction (1); ■ – [*Qiu, etc.*, 2009], ▲ – [*Curti and Degueldre*, 2002], ● – experimental values

In figure 3 results of calculation of temperature dependence of the equilibrium constant of the reaction (1) received based on the results of the present work at 150ºC as well as, on the results received by E.V. Iovleva at 250ºC [*Iovleva*, 2010] and on the data of Curti and Degueldre at 25ºC [*Curti and Degueldre*, 2002] are presented. In the same picture results of definition of solubility of a zirconium's dioxide in LiOH solutions ($m = 1\cdot10^{-4}$) [*Qiu, etc*., 2009] are presented.

We notice that the values calculated from the equation (4) differ from the results of Qiu and Guzonas [*Qiu, etc.,* 2009] work approximately by the same value (1.1±0.2). It is possible to assume that, most likely, the sample of the zirconium's dioxide, used in the work [*Qiu, etc.,* 2009], had essentially greater dispersion, than our sample. It is impossible to exclude also that great values of the solubilities received in the work [*Qiu, etc.,* 2009], are connected with the formation of negative-charged complexes: $Zr(OH)_5^-$ and (or) $Zr(OH)_6^{2-}$.

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