*Russian Journal of Applied Chemistry, Vol. 77, No. 7, 2004, pp. 1097–1099. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 7, 2004, pp. 1112–1115.*
*Original Russian Text Copyright © 2004 by Nagornyi, Kolyshkin, Vol'khin.*

# Mercury(II) Sorption on Nickel(II) Hydroxide: Influence of Halide Ion Concentration and pH of the Solutions

**O. V. Nagornyi, A. S. Kolyshkin, and V. V. Vol'khin**

*Perm State Technical University, Perm, Russia*

Received November 25, 2003

**Abstract**—Sorption of Hg(II) on β-$Ni(OH)_2$ was studied as influenced by chloride ion concentration and pH of the solutions, affecting the Hg(II) speciation. The sorption mechanism was considered.

Mercury(II) compounds are biologically hazardous. Mercury and its compounds are concentrated naturally by soil particles and mineral suspension and are accumulated in bottom sediments. Accumulation and transfer of mercury in the nature is largely controlled by adsorption [1].

Sorption is used to remove mercury compounds from aqueous solutions. Leikin *et al.* [2] used organic anion-exchangers as sorbents for negatively charged mercury halide complexes. Sorption of mercury(II) on natural minerals, kaolinite [3], goethite [4], and quartz [5], was studied.

Although many minerals can adsorb mercury compounds, only synthetic inorganic sorbents are efficiently used at present to remove mercury compounds from aqueous solutions. More than 90% of Hg(II) is removed with freshly prepared hydrated iron(III) oxide from aqueous solutions with pH from 5 to 8.6 [6]. A number of new inorganic sorbents including those for anionic complexes have been developed to date [7]. Nickel(II) hydroxide [8] and double nickel hydroxides with other metals [9] have relatively high anion-exchange capacity for Hg(II) complexes. Therefore, the study of synthetic inorganic sorbents for Hg(II) is an urgent problem.

The diversity of mercury species present in aqueous solutions complicates selection of inorganic sorbents for Hg(II). For example, in aqueous solutions containing $Cl^-$ anions, Hg(II) exists in the form of the following aqua, hydroxoaqua, and mixed hydroxoaquachloride or chloride complexes: $Hg^{2+}$, $HgOH^+$, $Hg(OH)_{2(aq)}$, $Hg(OH)_3^-$, $HgCl^+$, $HgCl_{2(aq)}$, $HgOHCl_{(aq)}$, $HgCl_3^-$, $HgCl_4^{2-}$ [1, 4, 10, 11]. Formation of cationic, neutral, and anionic mercury(II) species can result in incomplete mercury sorption from aqueous solutions. Neutral and anionic Hg(II) species are stable mainly at pH close to that of natural waters [1]. In this case, anion exchangers can be used as the sorbents. However, to determine the mechanism of Hg(II) sorption on metal hydroxides exhibiting anion-exchange properties, additional studies are required.

The aim of this work was to determine the influence of $Cl^-$ concentration and pH of the solution on Hg(II) sorption on nickel(II) hydroxide and to propose the sorption mechanism.

Nickel(II) hydroxide exists in α- and β-modifications. In this work we studied β-$Ni(OH)_2$. Both modifications have the layered brucite structure. The interlayer spacings in β-$Ni(OH)_2$ lattice are broadened owing to incorporation of $H_2O$ molecules ($c$ = 0.80 nm); the brucite layers in β-$Ni(OH)_2$ lattice are closer ($c$ = 0.46 nm) [12]. The α-modification is unstable and is unsuitable as a sorbent.

β-$Ni(OH)_2$ was prepared by exchange reaction of aqueous solution of $Ni(NO_3)_2$ with NaOH taken in a 5% excess. The resulting precipitate was washed with distilled water and granulated by freezing. To remove $NO_3^-$ impurity, the granulated material was treated with 0.1 M NaOH for a long time. The $NO_3^-$ content in the solid phase was determined by IR spectroscopy.

The sorption experiments under dynamic conditions were performed by the conventional methods [13].

Aqueous Hg(II) solutions were prepared from $Hg(NO_3)_2 \cdot H_2O$. Mercury halide complexes were synthesized by addition of aqueous solutions of KCl, KBr, and KI. All the salts were of analytically pure grade. The Hg(II) content in the solution was determined by absorption of the mercury complex with Crystalline Violet at $\lambda$ = 605 nm using a KFK-2MP photocolorimeter [14].

The relative content of different Hg(II) species formed at various concentrations of free $Cl^-$ was cal-

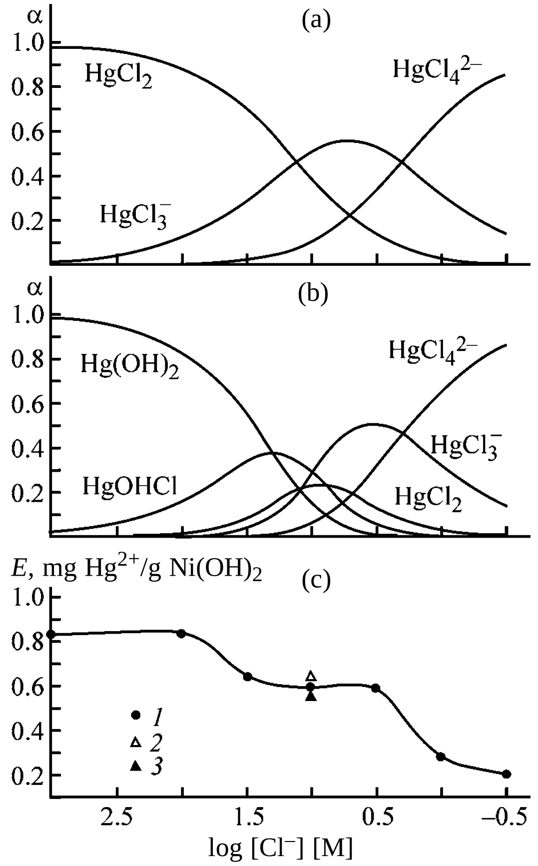

**Fig. 1.** (a, b) Mole fractions of Hg(II) species in solutions α and (c) sorption capacity of β-$Ni(OH)_2$ for Hg(II) *E* as functions of $[Cl^-]$. pH: (a) 5; (b) 9; (c) (*1*) ~5; (*2*) 7.8, kept for more than 24 h; and (*3*) 8.3, kept for more than 24 h.

culated from the equilibrium constants of the following reactions [15]:

$$Hg^{2+} + OH^- \rightleftarrows HgOH^+, \quad \log K = 10.6;$$

$$Hg^{2+} + 2OH^- \rightleftarrows Hg(OH)^0_{2(aq)}, \quad \log K = 21.8;$$

$$Hg^{2+} + Cl^- \rightleftarrows HgCl^+, \quad \log K = 7.2;$$

$$Hg^{2+} + 2Cl^- \rightleftarrows HgCl^0_{2(aq)}, \quad \log K = 14.0;$$

$$Hg^{2+} + 3Cl^- \rightleftarrows HgCl_3^-, \quad \log K = 15.1;$$

$$Hg^{2+} + 4Cl^- \rightleftarrows HgCl_4^{2-}, \quad \log K = 15.4;$$

$$Hg^{2+} + Cl^- + OH^- \rightleftarrows HgClOH^0_{(aq)}, \quad \log K = 18.1.$$

The results of these calculations for a solution with pH 5 are shown in Fig 1a. The dependence of the sorption capacity of β-$Ni(OH)_2$ for Hg, *E* [mg $Hg^{2+}$/g $Ni(OH)_2$], on the $Cl^-$ concentration varied in the same range is shown in Fig. 1c. The total Hg(II) concentration in each solution was $10^{-3}$ M.

The dependence of the relative concentration of Hg(II) species in the solution on $[Cl^-]$ does not correlate with the dependence of the sorption capacity of β-$Ni(OH)_2$ for Hg(II) on $[Cl^-]$. This was due to the difference in the pH of solutions used for the calculation and the experimental pH of the working solutions. When the initial solution passed through a sorbent bed, its pH increased to 8.5–9.0. We recalculated the dependence of the relative concentrations of Hg(II) species on $[Cl^-]$ at pH 9. The results are presented in Fig. 1b.

Comparison of the calculated and experimental dependences allows the following conclusions. The maximal sorption capacity *E* was observed in the $[Cl^-]$ range from $10^{-3}$ to $10^{-2}$ M, when $Hg(OH)_2$ and HgOHCl were formed. When these complexes started to transform into $HgCl_3^-$ and $HgCl_4^{2-}$, the first drop of *E* [from 20 to 15 mg $Hg^{2+}$/g $Ni(OH)_2$] occurred. At $[Cl^-]$ higher than $10^{-0.5}$ M, the sorption capacity *E* decreased again from 15 to 7–6 mg $Hg^{2+}$/g $Ni(OH)_2$. Under these conditions, hydroxo complexes $Hg(OH)_2$ and HgOHCl disappeared completely. Then *E* remained constant at the level of 5.0–5.5 mg $Hg^{2+}$/g $Ni(OH)_2$.

To explain these results, let us consider possible mechanisms of Hg(II) sorption by metal hydroxides.

Anionic complexes $HgCl_3^-$ and $HgCl_4^{2-}$ can be adsorbed by the ion-exchange mechanism:

$$\equiv Ni\text{–}OH + HgCl_3^- \rightleftarrows \equiv Ni\text{–}ClHgCl_2 + OH^-.$$

Halide anions $Cl^-$, $Br^-$, and $I^-$, being in equilibrium with $HgHal_3^-$ and $HgHal_4^{2-}$, are absorbed by the same mechanism. Previously we showed that chloride ions are exchanged with equivalent amount of OH groups of metal hydroxides. This process, however, makes an insignificant contribution. The sorption in the absence of Hg hydroxo complexes occurs by the anion-exchange mechanism.

An increased sorption capacity for hydrolyzed Hg(II) species is due to the different sorption mechanism. Sarkar *et al.* [3] showed that M–O–Hg bridges (where M is metal ion of the metal hydroxide) are formed in this case. Sorption of Hg(II) hydroxo complexes involves formation of surface intraspheric complexes ≡MOHgCl or $MOHgOHCl^-$, with the formation of the latter complex being more thermodynamically favorable. For example, log*K* of formation of ≡AlOHgCl and $\equiv AlOHgOHCl^-$ complexes in adsorption of Hg(II) on gibbsite is 6.64 and –0.50, respectively.

Thus, hydrolyzed Hg(II) species such as HgOHCl are sorbed on nickel(II) hydroxide owing to formation

Sorption of Hg(II) on Ni(II) hydroxide from solutions containing $Cl^-$, $Br^-$, and $I^-$

| Anion | $E$, mg $Hg^{2+}$/g $Ni(OH)_2$ | Hg(II) desorption, % |
|---|---|---|
| $Cl^-$ | 17.8 | 31 |
| $Br^-$ | 10.1 | 51 |
| $I^-$ | 2.42 | 98 |

of the surface intraspheric complex ≡NiOHgCl. At the same time, HgOHCl is not the major mercury species at almost any concentrations of chloride ions in the solution. We suggest that the concentration of this complex remains approximately constant during the sorption (buffer effect). The only question is the rate of this process. We found that formation of HgOHCl is completed during passage of the solution through an ion-exchange column. The sorption capacity did not noticeably change after an Hg(II) solution was allowed to stand at pH 7.8 and 8.3 prior to sorption for additional time (see Fig 1b, points *2* and *3*, respectively).

The decrease in $E$ at $[Cl^-] > 10^{-2}$ M remains unclear. We suggest that the presence of different anionic species in the solution interferes with the sorption via formation of Ni–O–Hg bonds. A change in the composition of the Hg(II) complex and a decrease in the equilibrium constant of its formation are also possible.

The results of this work show that Hg(II) sorption on Ni(II) hydroxide from solutions containing $Br^-$ and $I^-$ should decrease owing to formation of $HgHal_3^-$ and $HgHal_4^{2-}$ complexes. This assumption is confirmed by the experimental data presented in the table. The working solutions contained $10^{-3}$ M Hg(II) and $10^{-1}$ M $Hal^-$. Mercury was desorbed with 0.1 M NaOH. The data on Hg(II) sorption from a chloride solution are included in the table for comparison.

In the presence of $Br^-$ and $I^-$ in the solution, the probability of the ion-exchange sorption of Hg(II) increases and formation of intraspheric surface complexes is suppressed owing to stabilization of $HgBr_3^-$ and $HgBr_4^{2-}$ (p$K$ 19.7 and 21.0, respectively) and especially $HgI_3^-$ and $HgI_4^{2-}$ (p$K$ 27.6 and 29.8, respectively). As the contribution of ion-exchange sorption of Hg(II) by nickel(II) hydroxide increases, the fraction of desorbed mercury increases. In the experiments with chloride and bromide solutions, the Hg(II) desorption is 4.9–5.2 mg $Hg^{2+}$/g $Ni(OH)_2$, which correlates with the $E$ vs. $[Cl^-]$ dependence (Fig. 1c). Chloride and bromide anions can be involved in the ion exchange. The equilibrium $Hal^-$ concentrations in the solutions in the course of the sorption decrease in the following order: $Cl^- > Br^- > I^-$. Our experimental results show that the surface intraspheric Hg(II) complexes are stable in 0.1 M NaOH.

## CONCLUSIONS

(1) The dependence of Hg(II) speciation in solutions with pH 5.0 and 9.0 on the $Cl^-$ concentration was calculated.

(2) The dependence of the sorption capacity of $\beta$-$Ni(OH)_2$ for Hg(II) on $[Cl^-]$ was measured experimentally.

(3) The sorption capacity of $\beta$-$Ni(OH)_2$ for Hg(II) correlates with that calculated for solutions with pH 9.

(4) Ionic Hg(II) complexes can be absorbed by $\beta$-$Ni(OH)_2$ owing to exchange with OH groups of the hydroxide. The sorption mechanism of hydroxo Hg(II) complexes involves formation of surface intraspheric complexes like MOHgHal.

## REFERENCES

1. Stumm, W. and Morgan, J.J., *Aquatic Chemistry*, New York: Wiley, 1996.
2. Leikin, Yu.A., Tarasova, T.I., Tikhonova, L.A., and Musa, N., *Zh. Fiz. Khim.*, 1997, vol. 71, no. 2, pp. 321–323.
3. Sarkar, D., Essington, M.E., and Misra, K.C., *Soil Sci. Soc. Am. J.*, 2000, vol. 64, pp. 1968–1975.
4. Barrow, N.J. and Cox, V.C., *J. Soil Sci*, 1992, vol. 43, pp. 295–304.
5. MacNaughton, M.G. and James R.O., *J. Colloid Interface Sci.*, 1974, vol. 47, pp. 434–440.
6. Kinniburgh, D.G. and Jackson, M.L., *Soil Sci Soc. Am. J.*, 1978, vol. 42, pp. 45–47.
7. Kapustin, A.E., *Usp. Khim.*, 1991, vol. 60, no. 12, p. 2685.
8. Vol'khin, V.V., Tomchuk, T.K., and Leont'eva, G.V., *Zh. Prikl. Khim.*, 1983, vol. 56, no. 4, pp. 767–772.
9. Sokolova, M.M. and Vol'khin, V.V., *Zh. Neorg. Khim.*, 1997, vol. 42, no. 7, pp. 1091–1093.
10. Newton, D.W., Ellis, R., Jr., and Paulsen, G.M., *J. Environ. Qual.*, 1976, vol. 5, pp. 251–254.
11. Barnum, D.W., *Inorg. Chem.*, 1983, vol. 22, p. 2297.
12. Scheinost, A.C. and Sparks, D.L., *J. Colloid Interface Sci.*, 1999, vol. 223, p. 170.
13. Polyanskii, N.G., Gorbunov, G.V., and Polyanskaya, N.L., *Metody issledovaniya ionitov* (Methods for Studying Ion Exchangers), Moscow: Khimiya, 1976.
14. Tarayan, V.M., Ovsepyan, E.N., and Lebedeva, S.P., *Arm. Khim. Zh.*, 1970, vol. 23, no. 12, pp. 1085–1090.
15. Morel, F.M.M., Kraepiel, A.M.L., and Amyot, M., *Ann. Rev. Ecol. Systemat.*, 1998, vol. 29, p. 551.
16. Sokolova, M.M. and Vol'khin, V.V., *Zh. Neorg. Khim.*, 1997, vol. 42, no. 10, pp. 1631–1635.