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ANALYTICAL CHALLENGE

Solution to solubility product challenge

Anna Maria Michałowska-Kaczmarczyk[1] · Tadeusz Michałowski[2]

The winner of the solubility product challenge (published in volume 407/7) is

William E. Acree, Dept. of Chemistry, University of North Texas, Denton, TX, USA

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Our congratulations!

Solution

As mentioned previously [1], the solubility of nickel dimethylglyoximate (**NiL₂**) in water can be described by considering the equations for five equilibrium constants:

$$K_{a,HL} = [H^+][L^-]/[HL] \quad (1)$$

$$K_{sp} = [Ni^{2+}][L^-]^2 \quad (\text{for the precipitate } \mathbf{NiL_2}) \quad (2)$$

$$K_{2L} = [NiL_2]/\left([Ni^{2+}][L^-]^2\right) \quad (\text{for the soluble complex } NiL_2) \quad (3)$$

$$K_1^{OH} = [NiOH^+]/\left([Ni^{2+}][OH^-]\right) \quad (4)$$

$$K_w = [H^+][OH^-] \quad (5)$$

The numerical values for the relevant constants are $pK_{a,HL}=10.6$, $pK_{sp}=23.66$, $\log K_{2L}=17.24$, $\log K_1^{OH}=4.6$, and $pK_W=14.0$ [2].

The solubility (s, mol/L) of $\mathbf{NiL_2}$, is the total concentration of soluble nickel-containing species:

$$s = [Ni^{2+}] + [NiOH^+] + [NiL_2] \quad (6)$$

Applying Eqs. 1–5, from Eq. 6 we have

$$s = 10^{-pK_{sp}} \cdot \left(1 + 10^{\log K_1^{OH} - pK_w + pH}\right) \cdot \frac{1}{[L^-]^2} + 10^{\log K_{2L} - pK_{sp}} \quad (7)$$

Since an excess of pure $\mathbf{NiL_2}$ is introduced into pure water, the total ligand (L) concentration is twice that of the total nickel concentration. The resulting equality

$$[L^-] + [HL] + 2[NiL_2] = 2[Ni^{2+}] + 2[NiOH^+] + 2[NiL_2] \quad (8)$$

can be rearranged into

$$[L^-] \cdot \left(1 + [H^+]/K_{a,HL}\right) = 2K_{sp} \cdot \left(1 + K_1^{OH} K_w/[H^+]\right) \cdot \frac{1}{[L^-]^2} \quad (9)$$

and then we obtain

$$[L^-] = \left(2 \cdot 10^{-pK_{sp}} \cdot \frac{1 + 10^{\log K_1^{OH} - pK_w + pH}}{1 + 10^{pK_{a,HL} - pH}}\right)^{1/3} \quad (10)$$

As we see, $[L^-]$ is a function of pH. Then we formulate the charge balance [3]

$$2[Ni^{2+}] + [NiOH^+] + [H^+] - [OH^-] - [L^-] = 0 \quad (11)$$

which can be transformed into the function

$$z = z(pH) = 10^{-pK_{sp}} \cdot \left(2 + 10^{\log K_1^{OH} - pK_w + pH}\right) \cdot \frac{1}{[L^-]^2} + 10^{-pH} - 10^{pH - pK_w} - [L^-] \quad (12)$$

This article is the solution to the Analytical Challenge to be found at http://dx.doi.org/10.1007/s00216-014-8407-2

✉ Tadeusz Michałowski
michalot@o2.pl

[1] Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland

[2] Faculty of Engineering and Chemical Technology, Technical University of Cracow, 31-155 Cracow, Poland

where $[L^-]$ is expressed by Eq. 10. The value of z=0 at pH=pH_0, i.e., $z(pH_0)=0$. Using Excel, we find $pH_0=7.97$, according to zeroing procedure (see Table 1 and Fig. 1). From Table 1 and Eq. 6 we find $s=4.530\times10^{-7} + 1.683\times10^{-8} + 3.802\times10^{-7} = 8.50\times10^{-7}$ mol/L (see Table 1, row pH=7.97).

Since the molar mass of nickel is 58.69 g/mol, the molar solubility $s=8.50\times10^{-7}$ mol/L corresponds to 50 μg Ni per liter, which is in good agreement with the experimental observations of Claassen and Bastings [4]. In contrast, the 'textbook' solubility $s^*=8.18\times10^{-9}$ mol/L, calculated from the formula $s^*=(K_{sp}/4)^{1/3}$, differs significantly from $s=8.50\times10^{-7}$ mol/L.

Table 1

pH	$[L^-]$ Eq. 10	z Eq. 12	$[Ni^{2+}]$ Eq. 2	$[OH^-]$	$[NiOH^+]$	$[NiL_2]$ Eqs. 2, 3
7.95	2.163E-09	6.958E-08	4.676E-07	8.913E-07	1.659E-08	3.802E-07
7.96	2.180E-09	3.396E-08	4.602E-07	9.120E-07	1.671E-08	3.802E-07
7.97	2.198E-09	–1.911E-09	4.530E-07	9.333E-07	1.683E-08	3.802E-07
7.98	2.215E-09	–3.805E-08	4.459E-07	9.550E-07	1.695E-08	3.802E-07
7.99	2.233E-09	–7.448E-08	4.388E-07	9.772E-07	1.707E-08	3.802E-07
8	2.251E-09	–1.112E-07	4.319E-07	1E-06	1.720E-08	3.802E-07

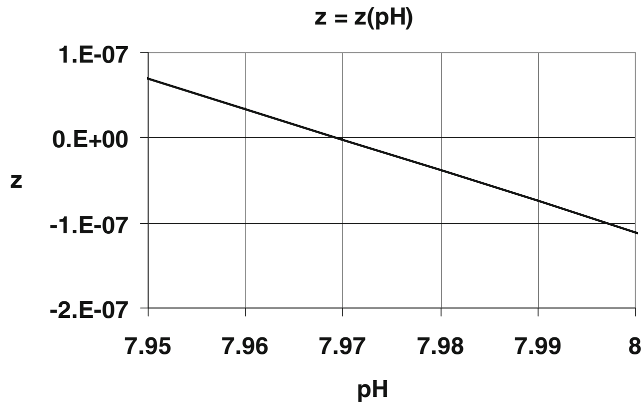

Fig. 1 Fragment of the z vs. pH relationship (Eq. 12)

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