ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 11, pp. 868–870. © Pleiades Publishing, Ltd., 2009.
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The Influence of a Water–Acetone Solvent on the Stability of Nickel(II) Complexes with Glycylglycine

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Received November 27, 2008

Abstract—The stability constants of nickel(II) complexes with glycylglycine in water–acetone mixtures (mole fraction of acetone X = 0–0.40) were determined by potentiometric titration at 298 K and an ionic strength of 0.1 M ($NaClO_4$). With an increase in the content of the organic cosolvent, nickel(II) glycylglycinates become more stable, mainly because of the better coordination of the ligand through the carboxy group.

DOI: 10.1134/S107032840911013X

To date, a number of regular features in the complexation thermodynamics of amines and their derivatives have been established from a great deal of experimental evidence [1]. To reveal the solvent effects on equilibrium processes involving charged species, we have studied complexation between transition metal ions and the simplest carboxylate ligands (acetate and glycinate ions) in mixed solvents [2, 3]. Here we continue our investigations in this area.

EXPERIMENTAL

Perchloric acid (reagent grade), glycylglycine (Fluka), sodium hydroxide (reagent grade), and acetone (reagent grade) were used without additional purification. Nickel(II) perchlorate (high-purity grade) and sodium perchlorate (high-purity grade) were recrystallized from water. A solution of sodium glycylglycinate was prepared from precisely weighed equimolar amounts of glycylglycine and carbonate-free saturated NaOH.

For potentiometric determination of the equilibrium constants of the complexation between nickel(II) and the glycylglycinate ion, we used a glass electrode, which has been reported to be effective in water–acetone mixtures [4]. A silver-chloride electrode served as a reference one. To reduce the diffusion potential at the ends of the electrolytic bridge, the inner solution of the reference electrode was prepared from a water–acetone solvent with the corresponding acetone content. Measurements were performed at 298 K and an ionic strength of 0.1 M ($NaClO_4$).

A potentiometric cell was charged with a solution of $Ni(ClO_4)_2$ (8.5 mmol/l) and $HClO_4$ (4.5 mmol/l) in aqueous acetone. A 0.7 M solution of sodium glycylglycinate was used as a titrant. The titrant was dosed by weight through a microsyringe.

The stability constants of the complexes were calculated from the titration data with the PHMETR program [5]. The dissociation constants of the glycylglycinium ion ($\mathbf{pK_1}$) and glycylglycine ($\mathbf{pK_2}$) in water–acetone, which were determined in a special experiment, were also employed in the calculations (Table 1). The errors in the determination of the stability constants were statistically estimated for a number of parallel measurements.

RESULTS AND DISCUSSION

Nickel(II) reacts with the glycylglycinate ion ($\mathbf{GG^-}$) to form 1 : 1 and 1 : 2 complexes [6]:

$$Ni^{2+} + GG^- \rightleftharpoons [NiGG]^+, \quad (1)$$

$$[NiGG]^+ + GG^- \rightleftharpoons [Ni(GG)_2]. \quad (2)$$

The stability constants of the complexes obtained in reactions (1) and (2) in aqueous solutions are in sufficiently good agreement with the literature data cited for comparable conditions (Table 2).

With an increase in the acetone content in the mixed solvent, both mono- and bisglycylglycinate complexes of nickel(II) become more stable, the increments of $\log K_{NiL}$ and $\log K_{NiL_2}$ (L stands for ligand) being virtually equal (Table 1). An analogous pattern has been observed for the stability constants of nickel(II) complexes with other carboxylate ligands in water–acetone mixtures [2, 3].

The large errors in the determination of the equilibrium constants of reaction (2) are due to the fact that potentiometric titration was stopped at a metal–ligand ratio of 1 : 1 because of precipitation initiated by further addition of the titrant at a high acetone content.

In some systems, acetone can act as both a solvent and a reagent toward a ligand [11]. For instance, in complexation between nickel(II) and ethylenediamine

Table 1. Dissociation constants of the glycylglycinium ion (pK_1) and glycylglycine (pK_2), the stability constants of nickel(II) glycylglycinate ($\log K_{NiL}$) and bisglycylglycinate ($\log K_{NiL_2}$), and the excess thermodynamic characteristics of the complexation ($\log K_i^E$) in water–acetone mixtures at 298 K and I = 0.1 mol/($NaClO_4$)

Constants	Acetone content (mole fraction) of the water–acetone solvent					
	0	0.05	0.10	0.20	0.30	0.40
$pK_1 \pm 0.03$	3.07	3.31	3.60	4.06	4.39	4.93
$pK_2 \pm 0.03$	8.12	7.89	7.76	7.63	7.49	7.52
$\log K_{NiL} \pm 0.04$	4.09	4.22	4.43	4.70	4.93	5.34
$\log K_{NiL_2} \pm 0.60$	3.53	3.85	4.10	4.10	4.43	
$\log K_i^E$	0	–0.03	0.03	–0.02	–0.10	0

in aqueous acetone, the stability constants calculated from experimental data are gross quantities, which reflect the interactions of the ligand with both the metal and the organic cosolvent. Because of this, the plot of $\log K$ vs. the acetone content of the water–acetone mixture for nickel(II) complexes with ethylenediamine passes through a maximum.

To ascertain the absence of a specific interaction between glycylglycine and acetone, we converted the stability constants of nickel(II) glycylglycinate to the excess scale using the equation [11]:

$$\log K_i^E = \log K_i - \log K_0 (1 - X_i/X_k) - \log K_k (X_i/X_k), \quad (3)$$

where X is the mole fraction of the organic component and K^E is the stability constant on the excess scale; the subscripts 0, k, and i refer to the initial, final, and current compositions of the solvent, respectively.

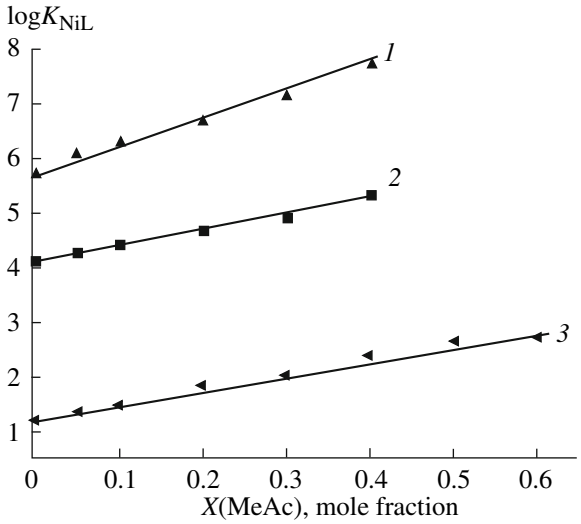
It is known that $\log K_i^E < 0$ when a solvent interacts with a ligand; for solvents forming stable solvate complexes with a metal, $\log K_i^E > 0$ [11]. For the complexation between nickel(II) and the glycylglycinate ion in water–acetone mixtures, $\log K_i^E$ tends to zero, which suggests the absence of any specific interactions of the reagents with the organic component of the solvent.

A comparison of the stability constants of $[NiGG]^+$ with those of nickel(II) complexes with the acetate (Ac^-) and glycinate ions (G^-) [3, 12] revealed that an increase in the acetone content of the solvent results in virtually equal increments of the stability constants of $[NiAc]^+$ and $[NiGG]^+$ (1.21 and 1.25 logarithmic units, respectively) and in a more considerable increment $\Delta \log K$ for $[NiG]^+$ (2.05 logarithmic units, figure).

When comparing the stability constants of $[NiAc]^+$, $[NiGG]^+$, and $[NiG]^+$ with the dissociation constants of acetic acid [12], the glycylglycinium ion, and the glycinium ion [13], we found that with an increase in the acetone content of the solvent to 0.40, the increments of the dissociation constants of acetic acid and the glycylglycinium ion are virtually equal (1.90 and 1.87 logarithmic units, respectively) and a relatively small (1.14

Table 2. Stability constants of the nickel(II) complexes with glycylglycine (NiL and NiL_2) in aqueous solutions

$\log K_{NiL}$	$\log K_{NiL_2}$	T, K; I, mol/l	References
4.09	3.53	298 K, I = 0.10 ($NaClO_4$)	This study
4.17	3.27	298 K, I = 0.12 (NaCl)	[7]
3.88	3.12	298 K, I = 0.10 (KNO_3)	[8]
4.11	3.21	298 K, I = 0.10 (KNO_3)	[9]
4.03	3.21	298 K, I = 1.00 ($NaClO_4$)	[10]



Plots of the stability constants of the nickel(II) complexes NiL vs. the acetone content of the water–acetone solvent: L = (*1*) G^- [3], (*2*) GG^-, and (*3*) Ac^- [12].

logarithmic units) for the glycinium ion. Therefore, the increments of the stability constants of the nickel complexes with acetate, glycinate, and glycylglycinate ions are inversely proportional to the increments of the acid dissociation constants of the corresponding ligands. Such a relationship between the increments of $\log K_{NiL}$ and pK_1 leads us to the conclusion that the complexes in water–acetone mixtures become more stable mainly because of the better coordination of the ligand through the carboxylate group.

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