Solution Equilibria of Alizarin Red S with Al(III) and Ni(II)

DAVID A. ROWLEY

Department of Chemistry, The George Washington University, Washington, D.C. 20052, U.S.A.

and JOHN C. COOPER*

Chemistry Division, U.S. Naval Research Laboratory, Washington, D.C. 20375-5000, U.S.A.

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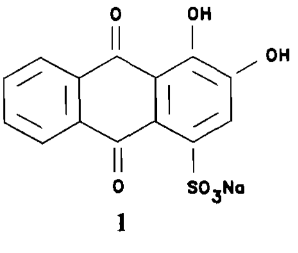
Abstract

The solution equilibria of Alizarin Red S (NaH_2-ARS, or 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracene sulphonic acid monosodium salt) with Al(III) and Ni(II) were investigated. A general procedure for speciation and the determination of equilibria was developed from work by Coleman *et al.* and Gampp *et al.* The results of the analyses gave a K_{H_2} for NaH_2ARS of $10^{5.71}$. For the Al(III)/Na_2-HARS equilibrium it was determined that a 1:2 complex was formed in solution with $\beta_2 = 10^{12.88}$. For the Ni(II)/NaH_2ARS equilibrium two species exist, a 1:1 and a 1:2 complex with $\beta_1 = 10^{5.35}$ and $\beta_2 = 10^{11.53}$.

Introduction

Alizarin Red S (NaH_2ARS or 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid monosodium salt) (1) has been used as a complexing agent for the analytical determination of a variety of metal ions including Al(III) [1, 2], Ni(II) [3–6], and Ga(III) [2]. Investigations of the solution equilibria of this ligand, with Ni(II) and other metal ions have produced conflicting results concerning speciation and equilibria which need to be resolved. In addition, NaH_2ARS has structural features of the enterobactin class of siderophores found in bacteria. These siderophores are responsible for iron transport in certain bacteria [7], and may be involved in other metal ion transport and concentration processes.



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This study focuses on the aqueous solution equilibria of H_2ARS^- including H_2ARS^- complexation of Al(III) and Ni(II). The solution protonation equilibria for ARS^{3-} are shown in eqns. (1) and (2).

$$ARS^{3-} + H^+ \rightleftharpoons HARS^{2-} \qquad K_{H_1} \qquad (1)$$

$$HARS^{2-} + H^+ \rightleftharpoons H_2ARS^- \qquad K_{H_2} \qquad (2)$$

Prior work [8] indicated that $\log K_{H_2} = 5.76$ and $\log K_{H_1} = 10.79$. Previous data on complex formation between Al(III) and NaH_2ARS indicates a 1:2 [2] or a 1:1 complex [1] while the data for Ni(II) indicates 1:1 complex formation [3, 4] or a mixture of 1:1 and 1:2 complexes [5, 6]. In these previous investigations no determination of speciation was made and no detailed analysis of the spectral data for the determination of the solution equilibria was undertaken. Therefore, these equilibria were investigated using Coleman's method for speciation [9] and quantitative determination of the solution equilibria was performed using methods developed by Gampp *et al.* [10, 11].

Experimental

Materials

Alizarin Red S (9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid monosodium salt) was purchased from Aldrich Chemical Company and was approximately 70% pure. The main inert ingredient is sodium sulfate. The NaH_2ARS was recrystallized twice from an acidified NaH_2ARS solution by the addition of a saturated solution of sodium chloride. This material was recrystallized from a 90% methanol solution. The resulting product contains one methanol of solvation and is stable to 300 °C. *Anal.* Calc. for $C_{15}H_{11}NaO_8S$: C, 48.13; H, 2.96; Na, 6.14; S, 8.57. Found: C, 48.09; H, 3.08; Na, 6.09; S, 8.81%. The molecular weight determined by pH titration was 370 g/mol (calculated molecular weight is 374).

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*Author to whom correspondence should be addressed.

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Al(III) solutions were prepared from a J.T. Baker 1000 ppm standard solution. All other chemicals were reagent grade or better and used without further purification. Sodium acetate/acetic acid and potassium dihydrogen phosphate/sodium phosphate were used for pH buffers at 4.38 and 7.01, respectively. Water used throughout was better than ASTM type I reagent water produced by a Milli-Q water purification system.

Measurements and Calculations

Spectrophotometric measurements were made with a Cary 118 UV–Vis spectrophotometer. All pH measurements were done with a Corning Model 130 pH meter equipped with a Corning 476216 combination electrode.

Speciation was determined by the method of Coleman *et al.* [9] using a program developed for that purpose. Equilibrium constants were calculated using program SPECFIT developed by Gampp *et al.* [10, 11] and adapted for HP1000 and VAX 11-750 computers. Equilibrium constants for NaH_2ARS were also determined potentiometrically by established methods.

Spectrophotometric measurements were made at 25.0 ± 0.1 °C in aqueous solution. The concentration range for NaH_2ARS and the metal ions was 10^{-6} to 10^{-4} M. Spectrophotometric data were obtained for a series of solutions in which the ligand concentration was held constant and the metal concentration varied. Measurements of the Al(III)/NaH_2ARS system were made at $pH = 4.38$ to avoid precipitation of the aluminum–hydroxy species. The Al(III)/NaH_2ARS complex did not form to an appreciable extent at $pH < 4$. Experiments at $pH = 7$ for the Ni(II) studies were chosen to optimize the formation of the Ni(II)/H_2ARS^- complex. The solutions were allowed to stand for at least two hours to insure that equilibrium was established.

Results and Discussion

Ligand protonation constants for NaH_2ARS are summarized in Table I. It can be seen that the K_{H_2} for NaH_2ARS measured potentiometrically and spectrophotometrically are in excellent agreement, as well as in agreement with the literature value. Analyses of the data for the pH range of 4 to 11 did not reveal any evidence for K_{H_1}. The solution spectra for NaH_2ARS display an isosbestic point at 453 nm when the $pH < 7$. Above $pH = 7$, the spectrum of NaH_2-ARS changes, and no isosbestic point is observed. The Coleman analyses of the spectra indicate that only two species are present between $pH = 4$ and $pH = 7$, as shown in Fig. 1. Note that for solutions in which the total concentration of NaH_2ARS is constant and the pH is varied, there should be a family of straight lines through the point (0,0) as is observed.

TABLE I. log K_{H_2} for NaH_2ARS

Literature [7]	5.76 ± 0.18
Potentiometric	5.70 ± 0.16
Spectrophotometric	5.71 ± 0.10

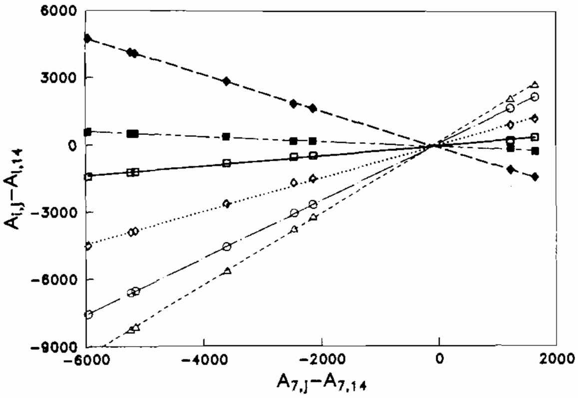

Fig. 1. Coleman plot for NaH_2ARS, pH = 4–7.

The solution chemistry of both Al(III) and Ni(II) was studied by the mole ratio method. The equilibrium model that was used for the Al(III)/NaH_2-ARS system is

$$HARS^{2-} + H^+ \longrightarrow H_2ARS^- \qquad K_{H_2}$$

$$Al^{3+} + 2HARS^{2-} \longrightarrow Al(HARS)_2^- \qquad \beta_2$$

The speciation test for the Al(III)/NaH_2ARS system shows a family of straight lines passing through the point (0,0). This indicates that only two species predominate in this equilibrium under these conditions. Analyses of the equilibrium concentrations show that 79.6% of the absorbing species is H_2ARS^- and 16.5% is $Al(HARS)_2^-$ and only 3.8% of the absorbing species is $HARS^{2-}$. Thus, only two species are predominant under the conditions of the experiment. In Table II are the formation constants for the systems studied, which were determined by the use of the SPECFIT program. The results of the SPECFIT analysis for $Al(HARS)_2^-$ are shown in Fig. 2.

TABLE II. Formation Constants of Metal Ions with NaH_2ARS

Species	log β
$Al(HARS)_2^-$	12.88 ± 0.01
Ni(HARS)	5.35 ± 0.14
$Ni(HARS)_2^{2-}$	11.53 ± 0.28

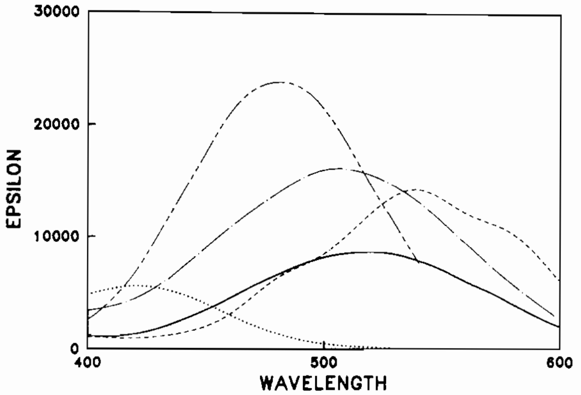

Fig. 2. Calculated spectra: $HARS^{2-}$ (——); H_2ARS^- (·······); $Al(HARS)_2^-$ (— - - —); Ni(HARS) (— — —); $Ni(HARS)_2^{2-}$ (-.-).

TABLE III. Spectral Data

Species	λ_{max} (nm)	ϵ
H_2ARS^-	421	5600
$HARS^{2-}$	519	8660
$Al(HARS)_2^-$	481	23860
Ni(HARS)	540	14320
$Ni(HARS)_2^{2-}$	506	16610

In the case of the speciation for Ni(II) and NaH_2ARS, the Coleman plot shows a family of straight lines, but these lines do not go through the point (0,0) indicating that more than two species are present. This was confirmed using the SPECFIT analysis (Fig. 2). The equilibrium model that was used for the analysis of the Ni(II) system is

$$HARS^{2-} + H^+ \longrightarrow H_2ARS^- \qquad K_{H_2}$$

$$Ni^{2+} + HARS^{2-} \longrightarrow Ni(HARS) \qquad \beta_1$$

$$Ni^{2+} + 2HARS^{2-} \longrightarrow Ni(HARS)_2^{2-} \qquad \beta_2$$

When conventional methods of analysis for the solution stoichiometry were used (mole ratio method and Job's Plot method) they gave results that indicated a 1:1 species in solution or inconclusive results. These seemingly contradictory results arise from the fact that both methods require strong complex formation which does not occur. Thus, care should be used when interpreting the results of Job's method or mole ratio methods when small equilibrium constants are obtained (*i.e.* $\log K < 6$) and data are obtained at low concentrations. The use of data analysis procedures such as SPECFIT is much superior.

Table III shows spectral data for the species studied.

The analyses described here provide significant corrections to previously reported formation and protonation constants, as well as the speciation. For Al(III) the correct value for $\log \beta_2$ is 12.88 (compared to previously reported 12.06 [2]). Also, the conclusion of Parker and Goddard [1] of a 1:1 complex for Al(III)/NaH_2ARS is in error. Complex formation between Ni(II) and NaH_2ARS is more complete. Govil and Banerji report formation of a 1:1 complex with $\log \beta_1 = 4.18$ and also describe [5] 1:1 and 1:2 complexes for Ni(II) and NaH_2ARS with $\log \beta_1 = 6.02$ and $\log \beta_2 = 9.43$. Our results clearly show that only two complex species are formed, with $\log \beta_1 = 5.35$ and $\log \beta_2 = 11.53$.

Conclusions

Both Al(III) and Ni(II) were found to form stronger complexes with Alizarin Red S than previously reported. The use of computer speciation calculations in conjunction with modern equilibrium calculation methods is effective in characterizing chemical systems not readily determinable by traditional graphical methods. The similarity of NaH_2ARS to the enterobactin class of siderophores and the higher than expected formation constants of Al(III) and Ni(II) with NaH_2ARS point to a likely role in metal ion transport by this class of siderophores.

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