

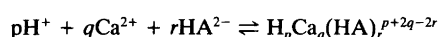
Potentiometric and Spectrophotometric Study of Calcium and Alizarin Red S Complexation

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Equilibria in the system H^+ , Ca^{2+} and Alizarin Red S have been studied by means of potentiometric (glass electrode) and spectrophotometric measurements in a 0.1 M NaCl medium at 25 °C. Calcium complexation is characterized by the formation of ternary species according to the reaction:



Equilibrium constants were evaluated within the range $3.3 \leq -\log[H^+] \leq 10.3$ and the wavelength interval $300 \leq \lambda \leq 700$ nm with the following results:

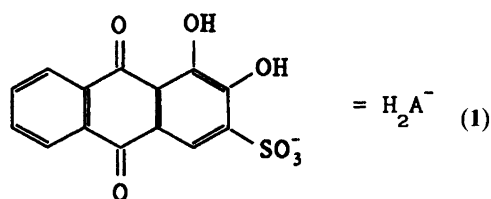
$$\log \beta_{012} = 8.04 \pm 0.04 \text{ (pot.)}; \quad \log \beta_{012} = 8.20 \pm 0.12 \text{ (spectr.)};$$

$$\log \beta_{-111} = -3.72 \pm 0.12 \text{ (pot.)}; \quad \log \beta_{-111} = -3.74 \pm 0.15 \text{ (spectr.)};$$

$$\log \beta_{-212} = -10.11 \pm 0.20 \text{ (pot.)}.$$

All errors reported are 3σ ($\log \beta_{pot}$). The protonation constants for Alizarin Red S were also determined. Data were analysed using the least-squares computer programs LETAGROPVRID (ETITR and SPEFO).

Sodium 1,2-dihydroxyanthraquinone-3-sulfonate (**1**), commonly known as Alizarin Red S (abbreviated as ARS in the following), is a well known chelating agent and its use as a colourimetric reagent for cations has been well established. The presence of two hydroxy groups in positions 1 and 2 with respect to the quinoid oxygen makes it very suitable for the formation of chelates with metal ions. The presence of a sulfonate group adds further reactivity to the molecule.



A number of studies have been carried out on the complexation of this ligand with various metal ions using both spectrophotometry and potentiometry. Among the earlier works on the chelates involving ARS, Leibhafsky and Winslow,¹ Raghava Rao and coworkers² and Larsen and Hirozawa³ were primarily concerned with the position of the chelate ring in the complex formed. Dey *et al.* studied the composition and stability of the complexes with copper, lead, chromium and hafnium.⁴⁻⁷ Later Varadarajulu *et al.* studied the stoichiometric and stability constants of che-

lates of ARS with certain metal ions.⁸⁻¹² Recently it has been reported that ARS, as a modifying agent, can achieve selective separation between different calcium minerals in a flotation process.¹³⁻¹⁵ ARS is found to react with the calcium sites at the mineral surface/water interface. The adsorption is generally combined with complexation in solution owing to the relatively high solubility of calcium minerals. Thus a study of surface complexation must include a separate investigation of calcium-ARS speciation in solution.

In the present paper detailed studies of the formation of calcium-ARS species as a function of $-\log[H^+]$, as well as protonation reactions of ARS, are reported, using both potentiometric and spectrophotometric techniques. Experimental data have been analysed with the least-squares computer programs LETAGROPVRID (ETITR and SPEFO).¹⁶

Experimental

Chemicals and analysis. Alizarinsulfonic acid sodium salt (Merck p. A.) and calcium chloride dihydrate (Merck p. A.) were without further purification. Stock solutions of ARS were prepared by dissolving the salt in a 0.1 M NaCl medium, whereas the calcium solutions were prepared by dissolution of $CaCl_2 \cdot 2H_2O$ in water, and a calculated amount of NaCl was added to keep the ionic strength at 0.1 M. For adjustment of $-\log[H^+]$, diluted solutions of so-

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dium hydroxide and hydrochloric acid were used. Both of these, as well as sodium chloride, were prepared from BDH concentrated solutions. HCl solutions were standardized against tris(hydroxymethyl)aminomethane and dilute NaOH solutions against freshly prepared and calibrated acid solutions. Deionized and degassed water was used for preparing all solutions.

The ligand concentrations were determined spectrophotometrically with a UV-visible spectrophotometer.

Apparatus. A Beckman DU-7 HS UV-visible spectrophotometer with a 1.00 cm quartz cell, together with a Corning 155 pH/ion meter, were used for combined spectrophotometric/ $-\log [H^+]$ measurements.

The automatic system for precise EMF titration and the electrodes have been described earlier.¹⁷

Methods. Experimental data were collected as series of spectrophotometric and potentiometric measurements at 25°C in a constant ionic medium of 0.1 M NaCl. In the spectrophotometric study, a series of solutions were prepared containing a certain amount of ARS with or without Ca^{2+} and with different total proton concentrations. After attaining equilibrium the absorbance values were measured within the wavelength range $300 \leq \lambda \leq 700$ nm. At the same time free proton concentrations were determined using a glass electrode, calibrated on a concentration scale. The observed absorbance, A_s , per unit path length at a particular wavelength, λ , is given by eqn. (1), where ϵ_i is

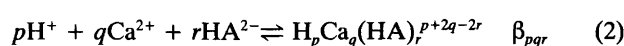
$$A_s = \sum \epsilon_i c_i \quad (1)$$

the molar absorption coefficient for the absorbing species i at the wavelength λ , and c_i is the concentration of the same species. Thus the spectrophotometric measurements give data (A_s , $-\log [H^+]$, H , B , C)_{nl}, where H , B and C denote the analytical concentrations of H^+ , Ca^{2+} and ARS, respectively.

The potentiometric measurements were carried out as series of titrations for which the total concentration of protons, H , was varied by adding known amounts of acid or base. The measurements and the calibrations of the electrode have been described earlier.¹⁷

The protonation constants of ARS were determined in separate measurements. The three-component equilibria, $H^+ - Ca^{2+} - HA^{2-}$, were studied in three ways: (1) at constant C/B ratios; (2) by titration of a certain amount of ARS, C , with calcium ion solutions at varying total proton concentrations, H ; and (3) as (2), but with a designed amount of calcium ions, B , titrated with ARS. The reproducibility and reversibility were tested by performing both forward titrations (starting at low $-\log [H^+]$ and adding base) and backward (decreasing $-\log [H^+]$ by addition of acid).

Data treatment. In the system $H^+ - Ca^{2+} - ARS$, the three-component equilibria have been assumed to have the gen-

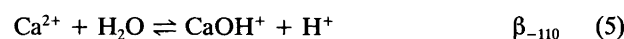


eral form of eqn. (2) together with the subsystems:

(i) the binary ARS equilibria



(ii) the hydrolytic equilibria of Ca^{2+}



The proton reactions of ARS were evaluated from separate potentiometric and spectrophotometric experiments, and the hydrolytic complex formed by calcium with the corresponding equilibrium constant was taken from the literature¹⁸ as $\log \beta_{-110} = -12.48$. In the evaluation of three-component experimental data, the equilibrium constants of subsystems (i) and (ii) were considered as known. Thus all the effects above this level were treated as being caused by the formation of three-component species.

Mathematical analysis of EMF data was performed with the least-squares computer program LETAGROPVRID (version ETITR).^{19,20} On treating the data, the pqr -triplets and the corresponding equilibrium constants that provided the 'best' fit to experimental data were determined by minimizing the error sum of squares $U = \sum (Z_{\text{calc.}} - Z_{\text{exp.}})^2$, where $Z_{\text{calc.}}$ and $Z_{\text{exp.}}$ denote the calculated and experimental values of $Z = (H - [H^+])/C$; H is the analytical concentration of H^+ , calculated over the level H_2O , Ca^{2+} and HA^{2-} , where $H = 0$.

In calculations on the combined $-\log [H^+]$ and spectrophotometric data the LETAGROPVRID version SPEFO was used, and $U = \sum (A_{s, \text{calc.}} - A_{s, \text{exp.}})^2$ was minimized. The appreciate error terms, denoted $\sigma(Z)$, $\sigma(A)$ and $3\sigma(\log \beta_{pqr})$ are defined and calculated according to Sillén.^{21,22}

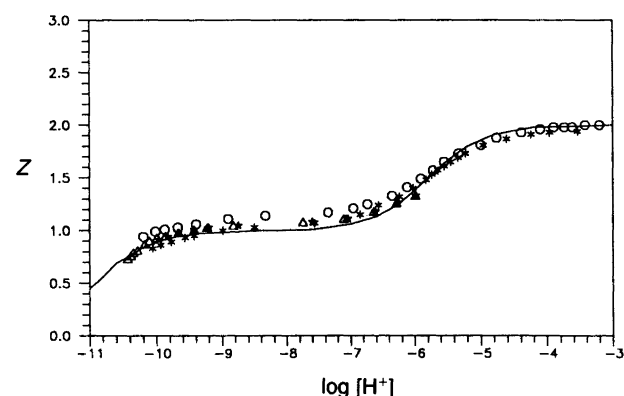


Fig. 1. Z versus $-\log [H^+]$ curves of potentiometric data from the $H^+ - ARS$ system. Different symbols are used to identify data from several independent titrations. The solid line was calculated using the constants $\log \beta_{101} = 5.79$ and $\log \beta_{-101} = -10.91$.

Data, calculations and results

The H^+ -ARS system. The investigation was started by recording UV-VIS spectra as a function of $-\log [H^+]$ to obtain a general view of the system and to select suitable wavelengths for computer evaluation. The data used to evaluate the acidity constants of ARS from spectrophotometric measurements comprised 38 experimental points and 380 absorbance values at 10 different wavelengths in the range 300–700 nm. The concentration ranges studied were $4 \times 10^{-5} \leq C \leq 2.5 \times 10^{-4} \text{ M}$ and $1.0 \leq -\log [H^+] \leq 13.0$. A computer calculation on these data ended at $\sigma(A_s) = 0.009$ giving $\log \beta_{101} = 5.74 \pm 0.01$ and $\log \beta_{-101} = -11.05 \pm 0.01$. The standard deviations $\sigma(A_s)$ at the reported wavelengths were all very small, thus indicating a good fit to the experimental data.

In order to provide a visual impression of the potentiometric data, Z versus $(-\log [H^+])$ curves were constructed, where Z is defined as the average number of protons reacted per A^{3-} . In this way, an indication of the accuracy of experimental data with respect to reversibility and reproducibility is obtained (Fig. 1).

Before the computer evaluation of EMF data started, a modification of the ARS concentration (weighed in) was made. This step is justified for the following two reasons: (i) Dissolving ARS in 0.1 M NaCl medium results in $-\log [H^+] = 6.0$, which is not in accordance with protonation constants obtained from the spectrophotometric measurements. The measured $-\log [H^+]$ indicates that the dissolved chemical is actually a mixture of Na_2HA and NaH_2A in a ratio of about 2:1. (ii) According to the definition, Z should reach a plateau value of 2 (corresponding to H_2A^-) at low $-\log [H^+]$ and approach zero (corresponding to A^{3-}) at high $-\log [H^+]$ values. However, the original curves did not exhibit this characteristic, but were shifted about 0.5 units upwards. After modification and recalculation of the concentration and composition of ARS according to the results from the spectrophotometric measurements, the Z versus $(-\log [H^+])$ curve in Fig. 1 was obtained and the protonation constants were evaluated.

Experimental data from potentiometric measurements, including four titrations yielding 195 titration points within the concentration ranges $7 \times 10^{-4} \leq 1 \times 10^{-3} \text{ M}$ and $3.5 \leq -\log [H^+] \leq 10.6$, were evaluated by the program LETAGROPVRID version ETITR, giving $\log \beta_{101} = 5.79 \pm 0.07$ and $\log \beta_{-101} = 10.91 \pm 0.07$. The standard deviation $\sigma(Z)$ was 0.06. In Fig. 1 the solid line is calculated using the aforementioned constants.

The H^+ - Ca^{2+} -ARS system. In this case the investigation also started by recording continuous spectra as a function of $-\log [H^+]$ for $C/B = 1$. The data used to evaluate the equilibrium constants from the spectrophotometric measurements comprised 43 experimental points at nine wavelengths within the region $300 \leq 700 \text{ nm}$, yielding 387 absorbance values. The concentration ranges studied were

$4 \times 10^{-5} \leq B \leq 2.5 \times 10^{-4} \text{ M}$, $4.5 \times 10^{-5} \leq C \leq 2.5 \times 10^{-4} \text{ M}$ and $3.6 \leq -\log [H^+] \leq 11$ with $0.25 \leq C/B \leq 4$. The results obtained were $\log \beta_{012} = 8.20 \pm 0.12$ and $\log \beta_{-111} = -3.74 \pm 0.15$ with the standard deviation $\sigma(A_s) = 0.03$.

The Z versus $(-\log [H^+])$ curves were constructed from titration data (Fig. 2). It can be noted that Z reaches a limiting value of 2 (corresponding to H_2A^-) in the absence of calcium, but takes lower values when metal ions are introduced owing to formation of species containing HA^{2-} . At high $-\log [H^+]$ values Z tends to zero, corresponding to A^{3-} , both in the free and complexed form.

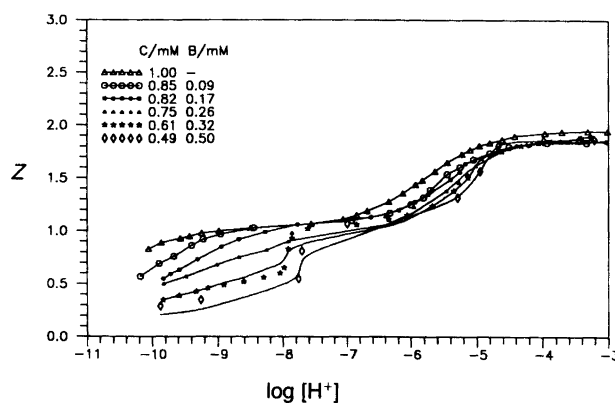


Fig. 2. Z versus $-\log [H^+]$ curves of potentiometric data in the H^+ - Ca^{2+} -ARS system. The solid lines were calculated using the constants proposed in Table 1. Here C and B denote the total concentrations of ARS and Ca^{2+} , respectively.

It may be mentioned that at $C/B = 1$ and concentrations $\geq 2.5 \times 10^{-4} \text{ M}$, precipitation of $CaHA(s)$ was observed in the range $5.5 < -\log [H^+] < 8.0$, which makes the experimental points in this area somewhat uncertain. However, by performing separate experiments involving filtration of the suspension, we have concluded that this precipitation has only a very small effect on the data evaluation.

The experimental data from potentiometric titrations were divided in two parts covering different $-\log [H^+]$ ranges. Data from the range $3.3 \leq -\log [H^+] \leq 5.9$ included six titrations yielding 202 experimental points. The measurements were performed by either adding ARS to calcium solutions having various $-\log [H^+]$ values or *vice versa*. In this way a large number of C/B ratios was covered. The calculations ended at $\sigma(Z) = 0.04$ with $\log \beta_{012} = 8.04 \pm 0.04$. Data from the range $4.9 \leq -\log [H^+] \leq 10.3$ comprised five titrations including 116 experimental points covering the ratios $1.5 \leq C/B \leq 10$ and the concentrations $8.8 \times 10^{-5} \leq B \leq 4.9 \times 10^{-4} \text{ M}$ and $6.1 \times 10^{-4} \leq C \leq 8.5 \times 10^{-4} \text{ M}$. The results obtained were $\log \beta_{-111} = -3.72 \pm 0.12$ and $\log \beta_{-212} = -10.11 \pm 0.20$ with $\sigma(Z) = 0.06$. These constants were used to calculate theoretical Z versus $(-\log [H^+])$ curves, which were combined with the experimental points in Fig. 2. The results from LETAGROP calculations are listed in Table 1.

Table 1. Results from final LETAGROPVRID calculations giving the formation constants for the 'best fitting' species. The formation constants are related according to reaction (2); when $3\sigma(\log \beta_{pq})$ terms are given the formation constants have been varied.

Method	Stand. dev. $\sigma(Z)/\sigma(A_b)$	H_2A^- $\log \beta_{101}$	A^{3-} $\log \beta_{-101}$	$Ca(HA)_2^{2-}$ $\log \beta_{012}$	CaA^- $\log \beta_{-111}$	CaA_2^{4-} $\log \beta_{-212}$
S	0.009	5.74 ± 0.01	-11.05 ± 0.01			
P	0.064	5.79 ± 0.07	-10.91 ± 0.07			
S	0.036	5.74	-11.05	8.20 ± 0.12	-3.74 ± 0.15	
P	0.042	5.79	-10.91	8.04 ± 0.04		
P	0.062	5.79	-10.91	8.04	-3.72 ± 0.12	-10.11 ± 0.20

^aS, spectrophotometry; P, potentiometry.

Table 2. Wavelengths of absorbance maxima, colour changes and corresponding species as a function of $-\log [H^+]$ for the system H^+-ARS and $H^+-Ca^{2+}-ARS$.

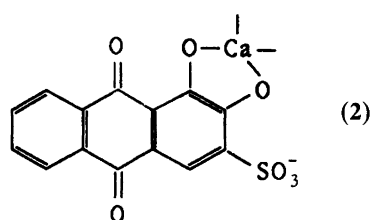
$-\log [H^+]$	λ_{max}/nm		Colour		Species	
	H^+-ARS	$H^+-Ca^{2+}-ARS$	H^+-ARS	$H^+-Ca^{2+}-ARS$	H^+-ARS	$H^+-Ca^{2+}-ARS$
1.0–5.5	420, 334	420, 334	Yellow	Yellow	H_3A, H_2A^-	
5.76–7.8	520, 334	520, 334	Red	Red	H_2A^-, HA^{2-}	$Ca(HA)_2^{2-}, HA^{2-}$
8.2	520, 334	540, 334	Red	Violet	HA^{2-}	$Ca(HA)_2^{2-}, CaA^-, HA^{2-}$
9.3–10.2	520, 334	555.5	Red	Violet	HA^{2-}	$CaA^-, CaA_2^{4-}, HA^{2-}$
10.4	540, 334	555.5	Violet	Violet	HA^{2-}, A^{3-}	CaA^-, CaA_2^{4-}
10.8–13.0	555.5	555.5	Violet	Violet	HA^{2-}, A^{3-}	CaA^-, CaA_2^{4-}

Discussion

The UV-visible absorption spectra of ARS in aqueous solutions show several pronounced peaks (Table 2). Obviously, λ_{max} shifts to longer wavelengths with increasing $-\log [H^+]$. The species HA^{2-} , which is predominant in the medium $-\log [H^+]$ range, exhibits two maxima at 334.5 and 520 nm. At high $-\log [H^+]$, i.e. the A^{3-} region, the maxima occur at 555.5 and 595 nm, while at low $-\log [H^+]$, H_2A^- displays $\lambda_{max} = 420$ nm.

An explanation for these large shifts has been suggested by Larsen and Hirozawa,² as resonance in the HA^{2-} molecule. They also pointed out that a similar resonance can be obtained when a metal ion reacts with ARS through the quinoid and alpha phenolic oxygen.

In the case of $M = Ca^{2+}$ this is obviously valid, since the species HA^{2-} and $Ca(HA)_2^{2-}$ exhibit similar spectra with equal λ_{max} . The species CaA^- , with the possible structure (2), exhibits the same λ_{max} as A^{3-} .

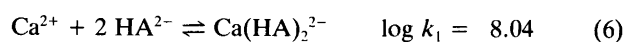


The shift in the λ_{max} values was also examined as colour changes. Table 2 gives λ_{max} , the corresponding species, and the colour change as a function of $-\log [H^+]$ for both H^+-ARS and $H^+-Ca^{2+}-ARS$ systems. From Table 2 it may be noticed that in the range $8.2 < -\log [H^+] \leq 10.8$, λ_{max} for the $H^+-Ca^{2+}-ARS$ system is constant at 555.5 nm, which is markedly different from that of the H^+-ARS system in the same $-\log [H^+]$ range. At other $-\log [H^+]$ values the λ_{max} seems to be more or less identical in the two systems. The reason for this observation lies in the stability of the violet-coloured complexes at $-\log [H^+] > 8.2$, while in other regions the colour change of ARS is dominant.

While the presence of $Ca(HA)_2^{2-}$ and CaA^- may be verified both from spectrophotometric and potentiometric measurements, CaA_2^{4-} could only be determined from EMF data, probably because the absorbance data contain too few points with high C/B ratios.

The existence of complexes having the general composition $M(HA)_2$, similar to $Ca(HA)_2^{2-}$, was previously proposed by Sangal¹⁰ for the Gd^{3+} , Tb^{3+} , Yb^{3+} and Lu^{3+} -ARS systems, and by Biryuk *et al.*^{11,12} for the Al^{3+} and Ga^{3+} -ARS systems. The species CaA^- and CaA_2^{4-} have their analogues in several other studies on Co^{2+} , Ni^{2+} and Be^{2+} -ARS systems.

Comparing reactions (6) and (7), it is evident that com-



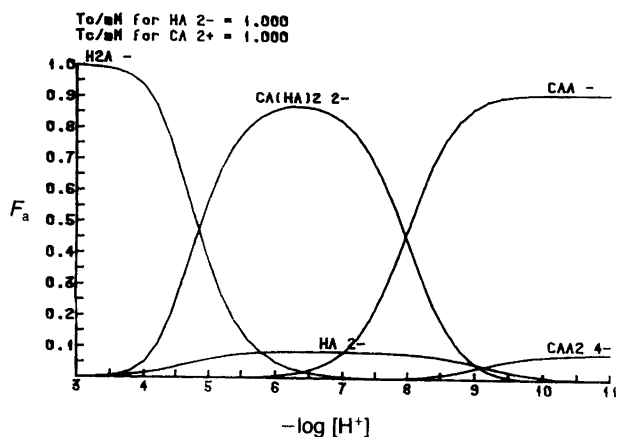


Fig. 3. Distribution diagram for the H^+ – Ca^{2+} –ARS system. F_a is defined as the ratio between HA^{2-} in a species and total ARS.

plexation through the phenolic oxygen seems to be much stronger, which may be another example of the well known stability of a five-membered ring.

Finally, in order to visualize the fractions of the different species as a function of $-\log [H^+]$, the computer program SOLGASWATER²³ (equipped with plotting procedures) was used to calculate the distribution diagram shown in Fig. 3.

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References

- Leibhafsky, H. A. and Winslow, E. H. *J. Am. Chem. Soc.* **60** (1938) 1776.
- Sarma, D. V. N. and Raghava Rao, Bh. S. V. *Anal. Chim. Acta* **13** (1955) 142; Venkateswarlu, K. S. and Raghava Rao, Bh. S. V. *Anal. Chim. Acta* **13** (1955) 79.
- Larsen, E. M. and Hirozawa, H. T. *J. Inorg. Nucl. Chem.* **3** (1956) 198.
- Mukherji, A. K. and Dey, A. K. *J. Indian Chem. Soc.* **34** (1957) 461.
- Mukherji, A. K. and Dey, A. K. *Proc. Natl. Acad. Sci. India*, **26 A** (1957) 20.
- Banerji, S. K. and Dey, A. K. *J. Indian Chem. Soc.* **38** (1961) 121.
- Banerji, S. K. and Dey, A. K. *Bull. Chem. Soc. Jpn.* **35** (1962) 2051.
- Varadarajulu, A. and Seshiah, U. V. *J. Indian Chem. Soc.* **48** (1971) 1065.
- Bartušek, M. *Collect. Czech. Chem. Commun.* **32** (1967).
- Sangal, S. P. *J. Prakt. Chem.* **36** (1967) 126.
- Biryuk, E. A., Nazarenko, V. A. and Ravitskaya, R. V. *Zh. Anal. Khim.* **23** (1968) 1658.
- Govil, P. K. and Banerji, S. K. *J. Chem. India* **10** (1972) 538.
- Fu, E. and Somasundaran, P. *Int. J. Miner. Process.* **18** (1986) 287.
- Xiao, L. and Somasundaran, P. *Miner. Metall. Process.* **May** (1989) 100.
- Wu, L. and Forsling, W. *J. Colloid Interface Sci.* *Submitted.*
- Ingri, N. and Sillén, L. G. *Ark. Kemi* **23** (1964) 97.
- Wu, L., Forsling, W. and Schindler, P. W. *J. Colloid Interface Sci.* *In press.*
- Smith, R. M. and Martell, A. E. *Critical Stability Constants*, Plenum Press, New York 1976.
- Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* **31** (1969) 353.
- Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* **31** (1969) 365.
- Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159.
- Sillén, L. G. and Warnqvist, B. *Ark. Kemi* **31** (1969) 341.
- Eriksson, G. *Anal. Chim. Acta* **112** (1979) 375.

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