

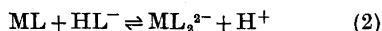
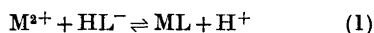
Stability Constants of Nickel and Zinc Chelates of Salicylaldehyde-5-sulphonic Acid in Aqueous Solution

SEIJA MIRTINEN, HEIKKI SAARINEN
and OSMO MÄKITIE

*Department of Inorganic Chemistry,
University of Helsinki, SF-00170 Helsinki 17,
Finland*

Derivatives of salicylaldehyde are very popular reagents in studies of the effects of substituents on metal chelate formation reactions. In a previous report from our laboratory, acid dissociation and copper(II) complex formation equilibria of salicylaldehyde-5-sulphonic acid were described.¹ Stability constants of nickel(II) and zinc(II) chelates of this watersoluble salicylaldehyde derivative are reported in this paper.

Potentiometric titration data for sodium salicylaldehyde-5-sulphonate in the presence of nickel and zinc ions reveal that the metal chelate formation reactions can be simply interpreted by assuming the occurrence of the successive chelation reactions:



The corresponding cumulative stability constants ($\beta_1 = [ML]/[M^{2+}][L^{2-}]$ and $\beta_2 = [ML_2^{2-}]/[M^{2+}][L^{2-}]^2$ at different ionic strengths (adjusted with potassium chloride) are presented in Tables 1 and 2. The thermodynamic values were determined by means of the Debye-Hückel equation:

$$\log \beta^\circ = \log \beta + \frac{4.072 \sqrt{I}}{1 + \alpha \sqrt{I}} - B I \quad (3)$$

Thermodynamic stability constants for the chelates and the values of the parameters α and B are collected in Table 3. In the case of nickel, the titration data reveal further that a third chelate is formed:



However, this chelate formation is so limited that accurate values cannot be obtained potentiometrically. An approximate value for the stability constant ($\beta_3 = [NiL_3^{4-}]/[Ni^{2+}][L^{2-}]^3$) at ionic strength 0.1 is 8.4.

Table 1. Stability constants of the nickel(II) chelates of salicylaldehyde-5-sulphonic acid in solutions of varying ionic strength (KCl) at 25°C.

<i>I</i>	Expt.	Calc. (eqn. 3)
	log β_1	
0.0070	4.12	4.12
0.0072	4.11	4.12
0.0820	3.67	3.67
0.106	3.63	3.60
0.206	3.42	3.45
0.603	3.23	3.23
	log β_2	
0.0071	6.71	6.69
0.0076	6.67	6.68
0.0819	6.18	6.21
0.106	6.15	6.14
0.205	5.98	5.97
0.601	5.74	5.74

Table 2. Stability constants of the zinc(II) chelates of salicylaldehyde-5-sulphonic acid in solutions of varying ionic strength (KCl) at 25°C.

<i>I</i>	Expt.	Calc. (eqn. 3)
	log β_1	
0.0113	3.24	3.25
0.0860	2.88	2.85
0.211	2.59	2.61
0.408	2.42	2.42
0.705	2.26	2.26
	log β_2	
0.0113	5.11	5.06
0.0860	4.55	4.63
0.211	4.39	4.40
0.408	4.32	4.25
0.705	4.15	4.18

As expected, the stabilities of the nickel(II) and zinc(II) chelates of salicylaldehyde-5-sulphonic acid are clearly lower than those of the copper(II) chelates, which is the normal order. Concentration stability constants of nickel and zinc chelates of salicylaldehyde-5-sulphonic acid have been reported earlier by Calvin and Melchior.² Their values log $\beta_1 = 3.79$ and log $\beta_2 = 6.56$ for the nickel(II) chelates and

Table 3. Thermodynamic stability constants of the chelates of salicylaldehyde-5-sulphonic acid (L) and the values of the parameters of eqn. (1).

Chelate	$\log \beta_1^\circ$	$\log \beta_2^\circ$	α	B
NiL	4.42		1.83	0.21
NiL ₂ ³⁻		6.99	1.52	0.33
ZnL	3.61		2.01	-0.11
ZnL ₂ ²⁻		5.43	1.43	0.42

$\log \beta_1 = 3.0$ (at an unspecified ionic strength and 25°C) for the first zinc(II) chelate can be compared with the values at low ionic strength found in this study. No other values seem to be available in the literature. The stabilities of the metal complexes of salicylaldehyde derivatives are linearly correlated with the acid strengths of the ligands.^{3,4}

Experimental. Sodium salicylaldehyde-5-sulphonate was prepared and purified as described earlier.¹ The nickel salt used was nickel(II) perchlorate from the G. Frederick Smith Chemical Co. The other reagents were of analytical grade.

The stability constants of the chelates were calculated using a modified SCOGS programme⁵ on a Burroughs B 6500 electronic computer. The equation used to calculate required values of the second dissociation constant of the ligand was:¹

$$pK_2 = 7.322 - \frac{2.036 \sqrt{I}}{1 + 1.577 \sqrt{I}} + 0.234 I$$

The other details of the procedure were the same as described earlier.¹

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Determination of the Bond Ruptured in the Alkaline Hydrolysis of Vinyl Acetate

ERKKI K. EURANTO and
ANTERO ALHONIEMI

Department of Chemistry, University of
Turku, Turku 50, Finland

It was recently confirmed in our laboratory by the oxygen-18 method that the acid-catalysed hydrolysis of vinyl acetate in dilute aqueous acid solutions takes place by acyl-oxygen fission^{1*} in accordance with kinetic results² but in contrast to earlier opinions based on oxygen-18 measurements.³ More recent results of Noyce and Pollack⁴ show without any doubt that vinyl acetate is hydrolysed by the A_{AC}2 mechanism in dilute acid solutions. There is some controversy about the site of bond fission in the alkaline hydrolysis of vinyl esters. Kiprianova and Rekasheva hydrolysed vinyl acetate and vinyl benzoate⁵ in alkaline aqueous solutions enriched in ¹⁸O and several vinyl esters with an excess of ¹⁸O in the ethereal or the ethereal and carbonyl oxygen atoms in alkaline solutions of normal isotopic composition.⁵ The results could not be interpreted without assuming that both vinyl-oxygen and acyl-oxygen fission takes place.^{3,5,6} On the other hand, the kinetics of the alkaline hydrolysis of vinyl esters does not differ significantly from that of corresponding saturated esters,⁵⁻⁷ and their hydrolysis mechanism is believed to be the normal B_{AC}2 mechanism.^{7,8}

To clarify this controversy, we determined the bond ruptured in the alkaline hydrolysis of vinyl acetate and, for comparison, ethyl acetate by the oxygen-18 method. The results are given in Table 1. The values of $R (=m(46)/m(44))$ in CO₂ from the formed acetate ion) obtained for vinyl acetate are in accordance with the value

* The expression for r on p. 1293 in Ref. 1 should be $\frac{1}{2}([A^*] + 2[A^{**}]) / \sum[A]$ rather than $\frac{1}{2}[A^*] / \sum[A]$ if the distribution of the oxygen isotopes is statistical. Because this is not the case, the correct way would have been to compare calculated and observed R values as is done in this paper. Because of the small excess of ¹⁸O in the water employed, the differences are insignificant and the conclusions drawn in Ref. 1 are unaffected.