STABILITY CONSTANTS OF 2-HYDROXY-1-NAPHTHALDEHYDE COMPLEXES*

A. BASCUNAN, R. CETINA and J. GOMEZ-LARA Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Mexico

(Received 5 June 1970)

Abstract—The stability constants of metal chelates of 2-hydroxy-1-naphthaldehyde have been determined. The results have been compared with existing data for similar ligands in terms of their double bond character. The large values of ΔS suggests a marked change in the solvation sphere of the actions.

INTRODUCTION

STABILITY constants for 2-hydroxy-1-naphthaldehyde complexes are known only for Cu(II) derivatives [1]. Here we report the stability constants of the Ba(II), Ca(II), Cu(II), Mg(II), Ni(II), Sr(II) and Zn(II) derivatives, determined by the potentiometric method at constant ionic strength, 0.3M in NaClO₄, in a 50:50 water dioxane mixture. Calculations were made applying the correction factors introduced by Van Uitert[2] to the Bjerrum's method[3]. The measurements were carried out at 15, 25, 35 and 50° in order to estimate the ΔG^o , ΔH^o and ΔS^o values for the complex formation reactions.

EXPERIMENTAL

All the chemicals were reagent grade, except for Ca and Ba perchlorates, which were prepared in solution from the corresponding carbonates and perchloric acid.

Potentiometric titrations were carried out using a Metrohm E-388 potentiometer with a combined EA-120-X glass electrode, calibrated against aqueous buffers at pH 4 and 7. A dioxane-water mixture, 50:50 was used as solvent. The determinations were made at 15, 25, 35 and 50° in a constant temperature bath ($\pm 0.02^\circ$). The glass electrode, a 2 ml microburette, a thermometer and a gas inlet tube bubbling nitrogen were introduced to the cell through a four hold rubber stopper. A typical solution to determine the pK_D of 2-hydroxy-1-naphthaldehyde was 0.01M in HClO₄, 0.02M in ligand and 0.3M NaClO₄ in 100 ml water-dioxane, 50:50. This solution was titrated with 1M aqueous NaOH. To determine the stability constants, the solutions contained also 2.5×10^{-3} M of the corresponding cation as perchlorate. In the case of Mn(11) it was not possible to otbain useful information due to immediate precipitation of a fine deposit at low pH.

RESULTS

In Table 1 the values of log K_1 , log K_2 and log β_2 are given for all the derivatives studied. The observed stability order is given by Cu > Ni > Zn > Mg > Ca \approx Ba > Sr as expected, except for the alkaline earth ions. The ratio log K_1/K_2 , as well as the magnitude of these constants, are within the limits expected by comparison with other similar systems, and show that structural factors related to the metallic ions are more important for the Cu and Ni derivatives.

*Contribution No. 328 from the Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Mexico.

- 1. M. Calvin and R. W. Wilson, J. Am. chem. Soc. 67, 2003 (1945); J. G. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, J. chem. Soc. 2001 (1958).
- L. G. van Uitert and C. G. Haas, J. Am. chem. Soc. 75, 451 (1953); L. G. van Uitert, C. G. Haas, W. C. Fernelius and B. E. Douglas, J. Am. chem. Soc. 75, 455 (1953).
- 3. J. Bjerrum, Metal Ammine Formation in Aqueous Solutions. Hasse, Copenhagen (1941).

Table 1. Stability constants of 2-hydroxy-1-naphthaldehyde metallic derivatives, determined from at least 3 different measurements. The deviation shown is never greater than $\pm 0.1 \log$ unit. ΔG in kcal/mole

			Temp		
Cation		15	25	35	50
	$\log K_1$	6.48	6.73	6.80	6.85
	$\log K_2$	5.13	5.41	5.50	5.59
	$\log \beta_2$	11.61	12.14	12-30	12.44
Cu	$\log K_1/K_2$	1.35	1.32	1.30	1.26
	$-\Delta G_1$	8.54	9.19	9.59	10.13
	$-\Delta G_2$	6.77	7.38	7.76	8 ·27
	$-\Delta G$	15-31	16.57	17.35	18-41
	$\log K_1$	4.57	4.63	4.66	4.85
	$\log K_2$	3.54	3.68	3.78	3-88
	$\log \beta_2$	8.11	8 ⋅31	8-44	8.73
Ni Zn	$\log K_1/K_2$	1.03	0.95	0.88	0.97
	$-\Delta G_1$	6.03	6.32	6.57	7.17
	$-\Delta G_{2}$	4.67	5.02	5.33	5.74
	$-\Delta G$	10.70	11.34	11.91	12.91
	$\log K_1$	3.86	3.87	3.90	4·01
	$\log K_2$	2.88	3.17	3.34	3.37
	$\log \beta_2$	6.74	7.04	7.24	7.38
Zn	$\log K_1/K_2$	0.98	0.70	0.56	0.64
	$-\Delta G_1$	5.09	5.28	5.50	5.93
	$-\Delta G_2$	3.80	4.32	4.71	4.98
	$-\Delta G$	8.89	9.60	10.22	10.91
	$\log K_1$	3.18	3.46	3.43	3.75
	$\log K_2$	2.63	2.73	2.89	3.02
	$\log \beta_2$	5.81	6·19	6.32	6.76
Mg	$\log K_1/K_2$	0.55	0.73	0.54	0.73
	$-\Delta G_1$	4.20	4·72	4.83	5.54
	$-\Delta G_2$	3-47	3.73	4.08	4.46
	$-\Delta G$	7.67	8 ∙45	8.91	10.00
	$\log K_1$	3.10	3.24	3.35	3.52
	$\log K_2$	2.48	2.61	2.71	2.81
	$\log \beta_2$	5.58	5.85	6.06	6.33
Ca	$\log K_1/K_2$	0.62	0.63	0.64	0 ·71
	$-\Delta G_1$	4.09	4.42	4.72	5-21
	$-\Delta G_2$	3.27	3.56	3.82	4 ∙15
	$-\Delta G$	7.36	7.98	8.54	9.36
	$\log K_1$	3.04	3.10	3.20	3.37
	$\log K_2$	2.47	2.56	2.64	2.72
	$\log \beta_2$	5.51	5.66	5.84	6.08
Sr	$\log K_1/K_2$	0.57	0.54	0.26	0.65
	$-\Delta G_1$	4.01	4.23	4.51	4.98
	$-\Delta G_2$	3.25	3.50	3.73	4.02
	$-\Delta G$	7.26	7.73	8 ∙24	9.00

		Temp., (°C)				
Cation		15	25	35	50	
	$\log K_1$	3.09	3.29	3.35	3.42	
	$\log K_2$	2.50	2.60	2.69	2.78	
	$\log \beta_2$	5.59	5.89	6.04	6.20	
Ba	$\log K_1/K_2$	0.59	0.69	0.66	0.64	
	$-\Delta G_1$	4·07	4·48	4.73	5∙0€	
	$-\Delta G_2$	3.30	3.55	3.80	4.12	
	$-\Delta G$	7.37	8.03	8.52	9.19	

Table 1 (Contd.)

A comparison of our results with those for similar systems is given in Table 2. The trend shown is acetyl acetonates > 2-hydroxy-1-naphthaldehydates > salicylaldehydates (columns *, ‡, ", Table 2), in agreement with their double bond character as defined by Calvin[1], irrespective of ionic strength of the medium. In the case of the salicylaldehyde complexes there are not enough data.

In Fig. 1 the values of $\log K_1$ and $\log K_2$ for some 2-hydroxy-1-naphthaldehyde derivatives are plotted against the corresponding values of the acetylacetonates determined in similar conditions. All the points lie on the same line, indicating that both ligands react in a similar way and the differences in the magnitude of the stability constants depend mostly on the character of the double bond.

The calculated values of ΔH_n and ΔS_n for the step, as well as for the total reactions, are listed in Table 3. The entropic term is always larger, as a direct result of the desolvation of the ions. Except for Zn(II), $\Delta S_1 > \Delta S_2$ indicates that the first step produces the more marked change in the solvation sphere of the cations. If one applies the Yatsimirskii relationship[4]



$\Delta S = 0 \cdot 1\Lambda M + \beta$

Fig. 1. Correlation of formation constants of acetyl acetone chelates [6] and 2-hydroxy-1naphthaldehyde chelates for Cu, Ni and Mg.

4. K. B. Yatsimirskii and V. P. Vasilev, Instability Constants of Complex Compounds p. 70. Van Nostrand, New York (1966).

Table 2. Comparison of stability constants for similar systems measured with and without constant ionic strength

Cation	*	†	‡	ş	11
Cu	22.59	21.21	16.08	12.34	13.31
Ni	17-40	14.63	11-36	8.51	9.19
Zn	17.20	14.05	9.54	7.24	8.10
Mg	13.58	10.65	7.30	6.39	6.80

*Stoichiometric stability constants for acetylacetonates measured without constant ionic strength at 30° C in dioxane water, 75:25 (v/v), Ref.[5].

 \dagger Thermodynamic stability constants for acetylacetonates determined in NaClO₄0.05M, at 25°C in dioxane water, 75:25 (v/v), Ref. [6].

 \pm Stoichiometric stability constants for 2-hydroxy-1napththaldehydates, without constant ionic strength, at 25°C in dioxane water, 75:25 (v/v), Ref.[7].

§This work.

"Stoichiometric stability constants for salycilaldehydates, without constant ionic strength, dioxane water, 50:50 (v/v), Ref. [8].

Table 3. Thermodynamic parameters calculated from log $\beta_2(\pm 0.1)$ at four temperatures

Cation	ΔS_1	ΔS_2	ΔS	$+\Delta H_1$	$+\Delta H_2$	$+\Delta H$
Cu	45	43	88	4.2	5.4	9.6
Ni	38	31	63	3.3	4.1	7.5
Zn	24	34	58	1.9	5.8	7.7
Mg	36	29	66	6.3	4.9	11.1
Ca	32	25	58	5-1	4.0	9.1
Ba	28	24	52	3.9	3.5	7.4
Sr	28	22	51	4·1	3.1	7 ∙2

to the overall values of ΔS , one obtains a slope of 0.12 with a correlation coefficient of 0.76, but if it is applied to ΔS_2 the slope is of 0.07 and the correlation coefficient is 0.83, whereas for ΔS_1 the relationship breaks down completely.

The large values for the entropic terms may be due to the contribution of three factors, the decrease in the number of particles, the reduction in the ionic nature of the medium as the complexes are formed and finally, the profound change in the solvation.

- 5. L. E. Maley and D. P. Mellor, Austr. J. Sci. Res. 2-A, 92 (1949).
- 6. G. A. Guter and G. S. Hammond, J. Am. chem. Soc. 81, 4686 (1959).
- 7. A. A. Sanchez, Thesis, Faculty of Chemistry, University of Mexico (1966).
- 8. D. P. Mellor and L. E. Maley, Nature, Lond. 161, 436 (1948).