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Thermodynamics of Metal Complex Formation in Aqueous Solution. X. A Calorimetric and Potentiometric Study of the Azide Complexes of Zinc(II)

STEN AHRLAND AND EFRAIM AVŞAR*

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The stability constants and the enthalpy changes for the formation of the azide complexes of zinc(II) have been determined in an aqueous medium of unit ionic strength with sodium perchlorate as a supporting electrolyte at 25.00 °C. The constants have been measured potentiometrically by means of an amalgam electrode, while the enthalpy changes were found calorimetrically. Four mononuclear complexes of moderate strength are formed. The first three steps are slightly endothermic, with a positive entropy change while the last step is exothermic, with a negative entropy change.

The studies of the thermodynamics of metal azide systems begun in the previous paper [1] of this series with nickel(II) is now continued with another divalent metal ion of mainly (a)-character, *viz.* zinc(II).

Like the previous investigations in this series,[1] the present one refers to a temperature of 25.00 °C and a medium of an ionic strength $I = 1.00$ M, with sodium perchlorate as the supplementary salt.

For this system, the most favourable method for the determination of the stability of weak complexes can be applied, *viz.* measurement of the free metal ion concentration, by means of the zinc amalgam electrode.

The stability constants have previously been determined potentiometrically by means of the dropping zinc amalgam electrode by Neves and Sant'Agostino [2] (at 25 °C and $I = 2.0$ M) and polarographically by Banerjea and Sing [3] at 25 °C and $I = 2$ M. However, no determination of the enthalpy changes connected with the complex formation seems to be reported so far.

EXPERIMENTAL

Chemicals. Sodium azide (B. D. H. and/or Merck) was purified and analyzed as described before.[1]

Zinc(II) perchlorate, zinc amalgam and sodium perchlorate were prepared and analyzed as before.[4] The Ag,AgCl electrodes were prepared according to Brown.[5]

Calculation of formation constants from potentiometric measurements of the free central ion concentration. The stepwise formation constants have been evaluated both graphically and numerically. The graphical method has been described before.[4] For the numerical calculations the least squares program "EMK" has been used.[6] This program minimizes the error square sum,

$$U(\beta_j) = \sum_{i=1}^{n} w_i (E_{M,i} - E_{M,i,\mathrm{calc}})^2$$

where w_i is the weight of individual observations, n the number of observations and $E_{M,i}$ the pertinent emf as defined before.[7] As the absolute random error in $E_{M,i}$ seems to be much the same for all points, these are given the same weight.

The potentiometric measurements. The emf of the following cell is measured:

$-\mathrm{Zn(Hg)}$	C_M M $\mathrm{Zn(ClO_4)_2}$ C_L M $\mathrm{NaN_3}$ $\mathrm{NaClO_4}$ to $I = 1.00$ M	1.00 M $\mathrm{NaClO_4}$	0.025 M NaCl 0.975 M $\mathrm{NaClO_4}$	Ag,AgCl +

* Present address: Technical University of Istanbul, Chemical Engineering Faculty, Department of Physical Chemistry, Macka-Istanbul, Turkey

A Leeds & Northrup 7555 Type K-5 potentiometer was used. The scale reading was reliable to ± 0.01 mV.

The measurements were arranged as titrations where the solutions in the left-hand half-cell were obtained by adding a known volume v (ml) of a solution T to $V_0 = 15.00$ ml of a solution S. The solutions S and T had the following compositions:

$$\text{S: } \begin{cases} C_M' \text{ M } Zn(ClO_4)_2 \\ (1.00 - 3C_M') \text{ M } NaClO_4 \end{cases} \qquad \text{T: } 1.000 \text{ M } NaN_3$$

Before and during the titrations the solutions were deaerated and mixed by a stream of purified nitrogen. To obtain the correct vapour pressure, the nitrogen was first bubbled through 1.00 M $NaClO_4$ solution. The potentials reached their equilibrium values very quickly, and the reproducibility was in general $\simeq 0.08$ mV for low ligand concentrations and even better for high concentrations.

In the same manner as before [7] it has been checked that the zinc amalgam electrode obeys Nernst's law.

Several difficulties arose in the measurements. First, the rapid dissolution of zinc amalgam in hydrazoic acid even at values of pH as high as $\simeq 5$ prevented the use of a buffered ligand solution. Also in the case of pure $Zn(ClO_4)_2$ solutions, the dissolution of zinc amalgam for low values of C_M was significant at values of pH $\lesssim 4$. For $C_M' = 5$ mM, and even for 10 mM, a steady decrease of emf was observed due to a gradual increase of C_M. At higher C_M' values, the dissolution of zinc amalgam was insignificant.

For this reason, an unbuffered ligand solution was used in the experiments, in spite of the fact that a perceptible hydrolysis of Zn^{2+} then takes place at high values of C_M. Five values of C_M' were used, *viz.* 10, 15, 20, 30 and 40 mM. For all series, the initial value of pH was about 5.

For $C_M' = 10$ mM, the initial pH was varied between 4.86 and 5.19 without any influence on the emf's. Consequently, no hydrolysis occurred.

For $C_M' = 15$ mM, two initial values of pH were used, 4.74 and 5.04. At a certain ligand concentration, hydrolysis set in and the solution became cloudy. At this point, the titrations were interrupted. Higher ligand concentrations could be reached without precipitation if large volumes were added directly and the equilibrium emf's measured before the slow formation of solid phase had had time to occur. Similar procedures were adopted also for all the series of higher C_M'. In order to minimize the errors due to the dissolution of the zinc amalgam electrode, the amalgam was added after the ligand solution and the emf then measured immediately. This could be done as the values of E_0' were very reproducible and therefore easy to determine separately.[7]

Both the graphical procedure and a curve-fitting program, executed by a high-speed computer, indicated four mononuclear complexes. Both methods gave almost the same value of the formation constants. The "EMK" program [6] which uses the directly measured potentials and the corresponding concentrations of metal and ligand as input data gave, on the other hand, slightly different values.

The calorimetric measurements. The calorimeter and the measurement technique have been described before.[8] Every titration series was in general carried out twice and the reproducibility was usually within 0.06 J.

A buffered ligand solution was used, in order to prevent the hydrolysis of zinc [9] during the titration. Although it is *per se* desirable to use high ratios of $C_H:C_I$ in order to suppress the hydrolysis as far as possible, very high ratios cannot be recommended because of the volatility of hydrazoic acid which easily causes the formation of explosive metal azides on various parts of the instrument. A leakage of acid will moreover affect the measured heats of reaction significantly. It is therefore advisable to work with low buffer ratios or preferably no buffer at all, if the hydrolysis is negligible.

In four of the eight titrations series, a buffered ligand solution was added to a solution of zinc perchlorate (Table 1, a–e). In order to reach the high ligand concentrations where the higher complexes are formed, reversed titrations were also performed. In these, zinc perchlorate solution was added to both buffered and unbuffered azide solutions (Table 1, e–h). Here, Q_{corr} is the heat change corrected for dilution, *i.e.* $Q_{corr} = (Q_{exp} - Q_{dil})$ and δQ_{corr} is the difference between the heat change calculated for each point from the ΔH_j and β_j of all the species involved and the experimentally measured heat change, *i.e.* $\delta Q_{corr} = (Q_{corr,calc} - Q_{corr})$.

The enthalpy changes have been calculated by the least squares computer program "Letagrop Kalle".[10]

RESULTS AND DISCUSSION

Data pertaining to the potentiometric measurements on the zinc(II) azide system are collected in Table 2.

The following sets of constants are calculated by the two procedures mentioned above:

Overall constants	Graphical and curve-fitting	"EMK"
β_1 (M^{-1})	5.48 ± 0.15	5.73 ± 0.60
β_2 (M^{-2})	18.0 ± 3.9	21 ± 12
β_3 (M^{-3})	147 ± 26	145 ± 60
β_4 (M^{-4})	254 ± 46	280 ± 90

The errors given correspond to three standard deviations. As can be seen, the errors given by

Table 1. The enthalpy data for the formation of the azide complexes of zinc(II). For all series: $V_0 = 90.00$ ml and $V = (V_0 + v)$ ml.

(a) S: $C_M = 20.00$ mM, $C_{NaClO_4} = 940.0$ mM and pH = 5.01
T: $C^\circ_L = 1000$ mM, $C^\circ_{HClO_4} = 200.0$ mM

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 0.719, 0.061; 6.00, 0.698, −0.059; 9.00, 0.811, −0.053; 12.00, 0.935, −0.000; 15.00, 0.981, 0.019; 18.00, 1.008, 0.056; 21.00, 0.955, 0.069; 24.00, 0.846, −0.002; 27.00, 0.765, −0.033.

(b) S: $C_M = 20.00$ mM, $C_{NaClO_4} = 940.0$ mM and pH = 4.28
T: $C^\circ_L = 1000$ mM, $C^\circ_{HClO_4} = 200.0$ mM

v (ml), $-Q_{corr}$(J), δQ_{corr} (J): 3.00, 0.595, −0.016; 6.00, 0.658, −0.096; 9,00. 0.796, −0.069; 12.00, 0.889, −0.047; 15.00, 0.896, −0.067; 18.00, 0.901, −0.051; 21.00, 0.875, −0.043; 24.00, 0.808, −0.050; 27.00, 0.738, −0.050.

(c) S: $C_M = 40.00$ mM, $C_{NaClO_4} = 880.0$ mM and pH = 5.04
T: $C^\circ_L = 1000$ mM, $C^\circ_{HClO_4} = 200.0$ mM

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 1.180, −0.001; 6.00, 1.303, −0.018; 9.00, 1.473, −0.005; 12.00, 1.668, 0.076; 15.00, 1.717, 0.067; 18.00, 1.743, 0.086; 21.00, 1.546, −0.078; 24.00, 1.453, −0.112; 27.00, 1.397, −0.094.

(d) S: $C_M = 60.00$ mM, $C_{NaClO_4} = 820.0$ mM and pH = 4.90
T: $C^\circ_L = 1000$ mM, $C^\circ_{HClO_4} = 200.0$ mM

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 1.620, 0.010; 6.00, 1.734, −0.026; 9.00, 1.933, −0.006; 12.00, 2.116, 0.038; 15.00, 2.223, 0.063; 18.00, 2.233, 0.045; 21.00, 2.191, 0.019; 24.00, 2.113, −0.017; 27.00, 2.025, −0.023.

(e) S: $C^\circ_L = 500.0$ mM, $C^\circ_{HClO_4} = 100.0$ mM, $C^\circ_{NaClO_4} = 600.0$ mM
T: $C_M = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM and pH = 4.24

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 2.399, 0.068; 6.00, 2.241, −0.004; 9.00, 2.150, −0.009; 12.00, 2.036, −0.025; 15.00, 1.914, −0.042.

(f) S: $C^\circ_L = 700.0$ mM, $C^\circ_{HClO_4} = 100.0$ mM, $C^\circ_{NaClO_4} = 400.0$ mM
T: $C_M = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM and pH = 4.24

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 2.545, 0.063; 6.00, 2.483, 0.025; 9.00, 2.468, 0.025; 12.00, 2.427, 0.011; 15.00, 2.382, 0.001.

(g) S: $C_L = 800.0$ mM, $C_{NaClO_4} = 200.0$ mM
T: $C_M = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM and pH = 4.24

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 2.602, 0.141; 6.00, 2.509, 0.035; 9.00, 2.514, 0.032; 12.00, 2.538, 0.051; 15.00, 2.532, 0.046.

(h) S: $C_L = 1000$ mM
T: $C_M = 100.0$ mM, $C_{NaClO_4} = 700.0$ mM and pH = 4.24

v (ml), $-Q_{corr}$ (J), δQ_{corr} (J): 3.00, 2.380, −0.033; 6.00, 2.423, −0.012; 9.00, 2.312, −0.142; 12.00, 2.378, −0.092; 15.00, 2.429, −0.054.

"EMK" are much larger than the errors of the other set. Since the input data to the curve-fitting procedure consist of the graphically estimated free ligand concentrations and the corresponding values [11] of X, any errors in the evaluation of the free ligand concentrations will not be introduced in the subsequent calculations. Consequently, smaller errors are likely to occur when this procedure is used.

Since a somewhat better fit to the calorimetric data is obtained from the estimates of the "EMK" program, this set of constants is considered as the "best" one.

The heat effects accompanying the complex formation are rather small. Therefore, fairly high Zn^{2+} concentrations have to be used, and the heats of dilution of participating species must moreover be determined very carefully. Further,

Table 2. Corresponding values of v, C_L and E_M for the zinc azide system.

C_M' (mM)→		10.00	15.00	20.00	30.00	40.00
v (ml)	C_L (mM)	E_M (mV)				
0.25	16.39	1.15	1.11	1.09	1.06	1.00
0.50	32.26	2.26	2.21	2.15	2.09	1.99
0.75	47.62	3.38	3.27	3.22	3.12	2.96
1.00	62.50	4.51	4.45	4.36	4.16	3.97
1.25	76.92	5.68	5.57	5.52	5.24	5.03
1.50	90.91	6.98	6.77	6.66	6.32	6.06
1.75	104.5	8.20	7.96	7.81	7.41	7.07
2.00	117.6	9.53	9.15	8.95	8.52	8.07
2.50	142.9	11.91	11.58	11.32	10.62	10.07
3.00	166.7	14.32	13.98	13.54	12.82	12.04
3.50	189.2	16.69	16.26	15.73	14.87	13.99
4.00	210.5	18.90	18.36	17.82	16.89	15.81
4.50	230.8	21.12	20.48	19.90	18.89	17.73
5.00	250.0	23.14	22.52	21.85	20.78	19.63
6.00	285.7	26.90	26.28	25.50	24.39	23.09
7.00	318.2	30.21	29.66	28.88	27.67	26.32
8.00	347.8	33.23	32.69	31.87	30.68	29.22
9.00	375.0	35.96	35.40	34.59	33.53	32.18
10.00	400.0	38.45	37.84	37.06	36.04	34.82
11.00	423.1	40.59	40.04	39.29	38.30	37.11
12.00	444.4	42.51	41.99	41.29	40.35	39.22
13.00	464.3	44.26	43.80	43.06	42.23	41.15
14.00	482.8	45.87	45.45	44.78	43.97	42.92
15.00	500.0	47.35	46.96	46.30	45.56	44.55
16.00	516.1			47.68	47.00	46.05

hydrazoic acid is formed, or dissociated, during the titrations. To correct for this, the values of K and $\Delta H°$ of the proton azide determined in the previous investigation [1] have been applied.

The thermodynamic functions of the azide complexes of zinc(II) are given in Table 3.

In spite of the difference of medium, our values of β_j agree fairly well with those reported by Neves and Sant'Agostino [2] ($\beta_1 = 6.0$ M^{-1}; $\beta_2 = 22$ M^{-2}; $\beta_3 = 220$ M^{-3}; $\beta_4 = 780$ M^{-4} at 25 °C and $I = 2$ M).

The enthalpy changes for the consecutive complexes of the zinc(II) azide system are all slightly endothermic, except the last step which is weakly exothermic. The complex formation between zinc and azide ions, with exception of the last step, is entropy stabilized which should be expected when the donors and the acceptors involved are hard.[12–14]

A striking feature of the azide system of zinc(II) is the abrupt increase of both $\Delta S°_j$ and $\Delta H°_j$ that takes place at the third step, but

Table 3. The overall formation constants and the values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$ for the consecutive steps of the azide complexes of zinc(II) at 25.00 °C and $I = 1.00$ M. The errors given correspond to three standard deviations.

j	β_j (M^{-j})	$-\Delta G°_j$ (kJ mol^{-1})	$\Delta H°_j$ (kJ mol^{-1})	$\Delta S°_j$ (J mol^{-1} K^{-1})
1	5.73 ± 0.60	4.33 ± 0.26	2.57 ± 0.30	23.1 ± 1.3
2	21 ± 12	3.2 ± 1.4	2.3 ± 1.7	19 ± 7
3	145 ± 60	4.8 ± 1.7	7.6 ± 2.3	42 ± 9
4	280 ± 90	1.6 ± 1.3	−6.5 ± 3.8	−16 ± 12

remarkably enough not at the second step as is the case for most zinc(II) systems. The reason for the discontinuities is probably changes of co-ordination taking place during the complex formation, so that the increased number of water molecules released will be reflected in the entropies. As the liberation of water is an endothermic process, similar discontinuities, though less marked, also are expected in the enthalpies. At these steps, the value of $\Delta S°_j$ will therefore be particularly high and $\Delta H°_j$ will be less exothermic, or more endothermic, than normally.[14]

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REFERENCES

1. Ahrland, S. and Avsar, E. *Acta Chem. Scand. A 29* (1975) 881.
2. De Almeida Neves, E. F. and Sant'Agostino, L. *Anal. Chim. Acta 49* (1970) 591.
3. Banerjea, D. and Sing, I. P. *J. Indian Chem. Soc. 39* (1962) 353.
4. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3692.
5. Brown, A. S. *J. Amer. Chem. Soc. 56* (1934) 646.
6. Karlsson, R. *Private communication.*
7. Ahrland, S., Avsar, E. and Kullberg, L. *Acta Chem. Scand. A 28* (1974) 855.
8. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3471.
9. Gubeli, A. O. and Ste-Marie, J. *Can. J. Chem. 45* (1967) 827.
10. Arnek, R. *Ark. Kemi 32* (1970) 81.
11. Fronæus, S. In Jonassen, H. B. and Weissberger, A. *Technique of Inorg. Chem.* Interscience, New York, London 1963, Vol. 1, Chapter 1.
12. Ahrland, S. *Helv. Chim. Acta 50* (1967) 306.
13. Ahrland, S. *Struct. Bonding (Berlin) 5* (1968) 118.
14. Ahrland, S. *Struct. Bonding (Berlin) 15* (1973) 167.

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