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Thermodynamics of Ion Association. XIII.[1a] Divalent Metal Succinates

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Potentiometric measurements at constant ionic strength have been used to identify the complex species present in solutions of copper succinate. Further measurements at low concentrations using cells with both hydrogen and glass electrodes have yielded thermodynamic equilibrium constants for the association of copper and zinc ions with the succinate ion in aqueous solutions at 25°. A sensitive differential calorimeter has been used to measure the enthalpies of formation of manganese, cobalt, nickel, copper, and zinc monosuccinate complexes, and the results are compared with those obtained from temperature coefficients of the association constants studied by a precise potentiometric method. ΔG, ΔH, and ΔS have been evaluated for the reaction $M^{2+} + A^{2-} \rightleftharpoons MA$ and all the available data for the dicarboxylate complexes are discussed.

Although potentiometric studies have been made of the extent of complexing in a number of divalent metal succinate solutions,[2] there are few thermodynamic data available for the copper and zinc systems.[3,4] The succinate ion is of special interest since, if both carboxylate groups are coordinated to the metal ion, the resulting complex contains a large, seven-membered ring. The comparatively small association constants may reflect a loss of the chelate effect but there is little doubt that the larger association constants for the formation of the corresponding oxalate and malonate complexes are consistent with ring formation in these cases.[5-7]

In order to assess the factors involved in the ion association process, it is necessary to know the entropy and enthalpy changes. Although values for the heats of formation of manganese, cobalt, and nickel succinates have been determined from the temperature coefficients of the association constants, the data are less reliable than those obtained by direct calorimetry. In the present work precise potentiometric measurements have been made with cells incorporating a glass electrode for copper succinate and a hydrogen electrode for zinc succinate. Heats of formation of manganese, cobalt, nickel, copper, and zinc monosuccinate complexes have been determined calorimetrically.

Experimental Section

Copper Succinate.—Grade A glassware and A.R. reagents were used whenever possible. The preparation and standardization of the copper perchlorate and sodium perchlorate solutions have been described elsewhere.[7] pH measurements were made at 25 ± 0.02° with a cell of the type

$$\mathrm{Ag}|\mathrm{AgCl},\ \mathrm{HCl}(0.2\ M)|\mathrm{glass}|\begin{matrix}\text{soln}\\ \text{under}\\ \text{study}\end{matrix}|\text{satd}\ \mathrm{KCl}|\begin{matrix}\text{calomel}\\ \text{electrode}\end{matrix}$$

Emf values measured with a Tinsley potentiometer using a Vibron electrometer (E.I.L. model 33B) as null detector were reproducible to ±0.1 mv. For constant ionic strength measurements, the electrode system was calibrated before and after each run using solutions of hydrochloric acid containing sufficient sodium perchlorate to give a final ionic strength of 0.2 *M*. Plots of emf against log $[H^+]$ showed good linearity, and unknown log $[H^+]$ values could be interpolated with an accuracy of ±0.003. At low concentrations, the electrodes were standardized with solutions of 0.01 *M* HCl + 0.09 *M* KCl (pH 2.078)[8] and with 0.05 *M* potassium hyrogen phthalate (pH 4.005).[9] Emf measurements were made in a nitrogen atmosphere with mixtures of copper perchlorate, sodium hydroxide, and succinic acid with or without sufficient sodium perchlorate to give a final ionic strength of 0.2 *M*.

Zinc Succinate.—Details of the cell design and electrode system used have been given previously.[10] Measurements at 25° were made of the emf of the cell

$$\mathrm{H_2,\ Pt}|\mathrm{H_2A,\ NaOH,\ ZnCl_2}|\mathrm{AgCl\text{–}Ag}$$

(H_2A = succinic acid).

Calorimetric Experiments.—The calorimeter used has been described previously.[11] Temperature changes were measured on dilution of about 10 ml of succinic acid–sodium succinate buffer with 300 ml of the metal chloride or perchlorate and with a potassium chloride solution of the same ionic strength. pH measurements were also made of the final solutions in both cases and corrections applied for changes in the concentrations of protonated and unprotonated anions. Concentrations were chosen such that only one complex, MA, was formed in the calorimeters.

Results and Discussion

In the concentration ranges used, the complex species to be expected in the succinate buffer solutions containing metal ions are MA and MHA^+. Previous studies have shown that in manganese and nickel succinate solutions both complexes were present, whereas for cobalt succinate the emf values could be satisfactorily interpreted in terms of only one complex, MA.

The concentrations of ionic species may be calculated from equations for total metal ion concentration

$$m_1 = [M^{2+}] + [MHA^+] + [MA]$$

for total succinic acid concentration

$$m_2 = [H_2A] + [HA^-] + [A^{2-}] + [MA] + [MHA^+]$$

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for electroneutrality

$$[\mathrm{Na}^+] + [\mathrm{H}^+] + 2[\mathrm{M}^{2+}] + [\mathrm{MHA}^+] = [\mathrm{HA}^-] + 2[\mathrm{A}^{2-}] + 2m_1$$

and for the thermodynamic dissociation constants for succinic acid

$$k_1 = [\mathrm{H}^+][\mathrm{HA}^-]f_1^2/[\mathrm{H_2A}]$$

$$k_2 = [\mathrm{H}^+][\mathrm{A}^{2-}]f_2/[\mathrm{HA}^-]$$

The required association constants are

$$K = [\mathrm{MA}]/[\mathrm{M}^{2+}][\mathrm{A}^{2-}]f_2^2$$

$$K_1 = [\mathrm{MHA}^+]/[\mathrm{M}^{2+}][\mathrm{HA}^-]f_2$$

and the ionic strength

$$I = 3m_1 - m_2 + 4[\mathrm{A}^{2-}] + [\mathrm{H_2A}] + 2[\mathrm{HA}^-]$$

Preliminary pH measurements were made with copper succinate solutions at a constant ionic strength of 0.2 M in order to determine the nature of the species present. Under these conditions, the activity coefficients may be omitted from the above equations and the corresponding equilibrium quotients are written K' and K'_1. The results, given in Table I, are consistent with the presence of only one complex, MA. Further experiments were made at low concentrations and the thermodynamic association constants, calculated by successive approximations for I,[10] are given in Table II. The value of K may be compared with 1.98×10^3 l. mole^{-1} obtained potentiometrically by Peacock and James.[3]

TABLE I

MEASUREMENTS AT CONSTANT IONIC STRENGTH, $I = 0.2\ M$

$10^3 m_2$, M	$10^3 m_1$, M	$10^3[\mathrm{Na}^+]$, M	$10^6[\mathrm{H}^+]$, M	$10^{-2}K'$ [a]
2.425	8.715	3.198	2.20_0	1.92
2.486	7.149	3.279	1.98_4	1.84
2.551	5.501	3.364	1.78_9	1.82
2.701	1.939	3.015	2.44_0	1.74
4.990	5.373	2.785	13.16_0	1.74

[a] Mean = $1.81 \pm 0.04 \times 10^2$.

TABLE II

COPPER SUCCINATE MEASUREMENTS AT $I \rightarrow 0$

$10^3 m_2$, M	$10^3 m_1$, M	$10^3[\mathrm{Na}^+]$, M	$10^6[\mathrm{H}^+]$, M	$10^3 I$, M	$10^{-3}K$ [a]
4.938	10.634	4.627	5.970	34.15	1.66
5.066	9.091	4.747	5.559	29.68	1.65
5.201	7.466	4.873	5.058	25.06	1.63
5.342	5.752	5.006	4.467	20.24	1.58
12.337	7.965	7.046	10.252	29.01	1.74

[a] Mean = $1.65 \pm 0.04 \times 10^3$.

For zinc succinate, it was necessary to take into account both MA and MHA$^+$; the concentration of ZnCl$^+$ could be ignored in view of the small association constant for its formation.[12] Various values of K_1 between 0 and 40 l. mole^{-1} were chosen and the corresponding K values, calculated by successive approximations using a KDF9 electronic computer, are given in Table III. The mean deviation in K passes through a minimum and the most appropriate value, $K_1 = 32$ l. mole^{-1}, may be compared with the corresponding values for nickel and manganese succinate of 20 and 15 l. mole^{-1}, respectively.[2] Using this value of K_1, thermodynamic values were evaluated, and the results are summarized in Table IV. The mean value of K at 25°, 2.94×10^2 l. mole^{-1}, is close to that reported at an unspecified ionic strength by Gelles and Hay,[4] 3.16×10^2; the only other literature value, 78 l. mole^{-1}, was obtained at an ionic strength of 0.2 M.[13]

TABLE III

ZINC MONOSUCCINATE ASSOCIATION CONSTANTS AT 25°

K_1	1.0	10.0	25.0	30.0	32.0 [a]	35.0	40.0
$10^{-2}K$	2.10	2.34	2.75	2.89	2.94 [a]	3.02	3.15
Dev. in K, %	3.09	2.56	2.00	1.64	1.53	1.57	1.59

[a] Value of K_1 chosen at 25°.

TABLE IV

ASSOCIATION IN SOLUTIONS OF ZINC SUCCINATE AT 25°; $K_1 = 32$

$10^3 m_2$, M	$10^3 \cdot [\mathrm{Na}^+]$, M	$10^3 \cdot m_1$, M	$10^3 \cdot [\mathrm{H\bar{A}}]$, M	$10^3 \cdot [\mathrm{A}^{2-}]$, M	$10^3 \cdot [\mathrm{MA}]$, M	$10^4 \cdot [\mathrm{MHA}^+]$, M	10^{-2} K [a]
3.8320	6.2166	6.7556	1.2281	1.6488	0.7855	1.2302	2.84
6.5192	10.9539	8.2814	1.7833	3.0360	1.4568	1.8772	2.94
3.9276	6.4900	7.0177	1.1635	1.7338	0.8714	1.1908	2.96
3.6495	6.0743	6.2751	1.0499	1.6681	0.7961	0.9832	3.00

[a] Mean $K = 2.94 \times 10^2$.

The results of the calorimetric experiments are summarized in Table V, in which ΔH_i is the heat change per mole of complex and ΔH_0 the heat of association corrected to $I = 0$.[14]

TABLE V

CALORIMETRIC RESULTS AT 25°

$10^3 m_1$, M	$10^3 m_2$, M	$10^2 I$, M	$10^4[\mathrm{MA}]$, M	ΔH_i, kcal mole^{-1}	ΔH_0, kcal mole^{-1}
Manganese Succinate					
5.1037	6.8552	3.135	9.987	2.89	3.38
5.2186	7.0009	3.198	9.896	2.53	3.02
4.6284	12.4341	4.568	13.322	2.26	2.82
5.4610	14.6700	5.361	16.469	2.27	2.87
4.8762	13.0993	4.806	13.800	2.42	3.00
Mean $\Delta H_0 = 3.02 \pm 0.15$ kcal mole^{-1}.					
Cobalt Succinate					
4.3360	7.1390	3.074	9.086	2.79	3.27
4.2430	6.3775	2.845	8.289	2.75	3.22
4.0291	7.8797	3.205	9.029	2.78	3.27
3.8061	6.8672	2.876	8.011	2.47	2.94
3.9456	7.1027	2.973	8.412	2.55	3.03
Mean $\Delta H_0 = 3.15 \pm 0.13$ kcal mole^{-1}.					
Nickel Succinate					
3.3603	9.8928	3.546	10.570	2.21	2.72
3.9370	9.8206	3.637	12.013	1.81	2.33
3.1316	8.8796	3.218	9.474	2.16	2.65
3.1278	7.6511	2.873	8.968	2.14	2.61
4.4797	9.1286	3.555	13.115	1.79	2.30
4.5302	8.6696	3.441	12.688	1.62	2.13
Mean $\Delta H_0 = 2.46 \pm 0.20$ kcal mole^{-1}.					
Copper Succinate					
1.2062	3.7402	1.211	6.059	4.26	4.58
1.2803	3.9704	1.272	6.933	4.33	4.66
1.2332	2.5497	0.8896	5.225	4.12	4.40
1.2383	2.5601	0.8976	5.045	4.29	4.58
Mean $\Delta H_0 = 4.56 \pm 0.07$ kcal mole^{-1}.					
Zinc Succinate					
2.8607	3.8752	1.736	6.276	4.08	4.48
3.1678	5.7216	2.295	7.318	3.83	4.27
3.1435	5.6778	2.278	7.277	4.05	4.49
3.1108	7.0234	2.644	8.006	3.84	4.31
Mean $\Delta H_0 = 4.39 \pm 0.10$ kcal mole^{-1}.					

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The available thermodynamic functions for the formation of the divalent metal monooxalate,[15] monomalonate,[15] and monosuccinate complexes are collected in Table VI, in which ΔH_T and ΔH_C refer to temperature coefficient and calorimetric data, respectively; the entropy changes have been calculated from ΔH_C. The good agreement between ΔH_T and ΔH_C indicates that reliable thermodynamic data can be obtained where a sufficiently large temperature range is used.

Table VI

Thermodynamic Functions

Reaction	ΔH_C, kcal mole^{-1}	ΔH_T, kcal mole^{-1}	$-\Delta G$, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}	ΔS_{hyd} (MA), cal deg^{-1} mole^{-1}	Ref
Metal Oxalates						
$Mn^{2+} + A^{2-}$	...	1.42	5.41	22.9	−54.8	5
$Co^{2+} + A^{2-}$	...	0.59	6.54	23.9	−55.8	5
$Ni^{2+} + A^{2-}$	...	0.15	7.05	24.2	−56.1	5
$Cu^{2+} + A^{2-}$	−0.05	...	8.49	28.3	−52.5	7
Metal Malonates						
$Mn^{2+} + A^{2-}$	3.68	3.53	4.48	27.4	−57.5	6, 14
$Co^{2+} + A^{2-}$	2.90	2.57	5.13	27.0	−59.8	6, 14
$Ni^{2+} + A^{2-}$	1.88	1.77	5.60	25.0	−62.8	6, 14
$Cu^{2+} + A^{2-}$	2.85	...	7.69	35.4	−52.6	6
$Zn^{2+} + A^{2-}$	3.13	3.06	5.22	28.0	−61.6	*a*, 6
Metal Succinates						
$Mn^{2+} + A^{2-}$	3.02	2.95	3.09	20.5	−64.2	
$Co^{2+} + A^{2-}$	3.15	2.81	3.02	20.7	−65.9	
$Ni^{2+} + A^{2-}$	2.46	2.23	3.20	19.0	−68.7	
$Cu^{2+} + A^{2-}$	4.56	...	4.42	30.1	−55.5	
$Zn^{2+} + A^{2-}$	4.39	...	3.36	26.0	−64.3	

[a] V. S. K. Nair, *J. Chem. Soc.*, 1450 (1965).

The heats of formation of the metal dicarboxylate complexes are predominantly endothermic since the Coulombic forces between the charged centers will vary with temperature in the same way as the macroscopic dielectric constant of water.[16] In spite of this unfavorable enthalpy change, the complexes are stabilized by the relatively large positive entropy changes due to the liberation of water molecules from the ions accompanying complex formation.

The entropies of hydration of the complexes given in Table VI have been calculated by the method described previously.[2] The values follow the order oxalate > malonate > succinate and may reflect an increasing polarity of the complexes associated with reduced stability.

The crystal fields produced by oxygen-coordinating ligands are quite similar to those of the water molecules, and so ΔH will not be much affected by ligand field stabilization. Nevertheless, for the most stable oxalate complexes, the enthalpies of formation vary in the expected direction. With the exception of manganese and cobalt succinates, the association constants for all the dicarboxylate complexes follow the Irving–Williams order of stability. It is clear from Table IV, however, that this cannot be explained entirely on the basis of crystal field stabilization by assuming that $-\Delta G$ depends only upon $-\Delta H$. Both copper monomalonate and monosuccinate complexes are formed with abnormally large endothermic heat changes. With this cation, additional stabilization is possible due to tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect. The resulting four short bonds in the *xy* plane and two long bonds in the *z* direction[17] may affect the thermodynamic functions in two ways:[18] (i) The increased covalent nature of the shortened M–ligand bonds in the *xy* plane will result in a more exothermic heat of formation. (ii) The accompanying closer contact of metal ion and charged coordinating sites in the ligand will lead to a more positive entropy of formation. At the limit of distortion a change of coordination from six in the aquo ion to four in the complex will also result in a more positive entropy of formation, but in this case an increased endothermicity will be expected due to the breaking of metal–water bonds.

In Table VI, it is seen that the abnormally large entropies of formation of both copper monomalonate and copper monosuccinate are accompanied by large endothermic heat changes rather than the exothermic heat changes required by (i) above. The data are consistent with the hypothesis that a larger number of water molecules are released in the process of complex formation with a change of coordination number of the copper(II). The increasing endothermicity of copper oxalate < malonate < succinate may reflect the increasing strain introduced in the ligand molecules in bringing the coordinating groups into bonding in the *xy* plane. In contrast to the behavior of the malonate and succinate complexes, the increase in stability in going from nickel(II) to copper(II) monooxalate is due to a more favorable heat, as well as a small positive entropy change.

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