The Stabilities of Metal Chelate Compounds formed by Some Heterocyclic Acids. Part II. Studies in Aqueous Dioxan.*

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Stability constants are reported for some chelated compounds with metals formed by picolinic, 6-methylpicolinic, and quinoline-2- and -8-carboxylic acid in 50% (v/v) dioxan–water, the method used being that of potentiometric titration. The results conform with those previously obtained in aqueous solution, although not always exactly.

IN Part I * stoicheiometric stability constants were reported for chelated compounds formed by a few metals with picolinic, 6-methylpicolinic, and quinoline-2- and -8-carboxylic acid in aqueous solution. Where the solubility of the complexes permits, the evaluation of stability data in such a medium rests on a sounder theoretical foundation than when solvents such as dioxan–water mixtures must be used. Since in our case some of the complexes were but slightly soluble in water, stability constants were also obtained in 50% (v/v) dioxan–water. Although the interpretation of data from this medium is uncertain, much useful information may be obtained by making assumptions as to the corrections to be employed. Such corrections have been made, especially by Van Uitert and Haas (*J. Amer. Chem. Soc.*, 1953, **75**, 451), but the corrections we have used rest on a rather different theoretical foundation, although they lead to quantitatively similar results. One of the main difficulties is that of interpreting pH meter readings in such a medium. The situation, as far as effective ionic concentrations is involved, is markedly changed by the non-polar solvent, and in particular the approximation $[H^+] = a_{H^+}$, justifiable in dilute aqueous solution, can no longer be used. The Debye–Hückel limiting law or the comprehensive data of Harned and Owen (" Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 29th edn.) could be used to correct for the increases in association, both for the hydrogen ion and for the other factors necessary in the calculations of $\bar{n}$ and $[L^-]$; this would lead to thermodynamic stability constants, but the corrections are not readily made, especially when metal ions are involved. No advantage would be gained in the present work by attempting to derive such thermodynamic data, especially when the figures obtained in water previously were stoicheiometric.

There is need, however, for calibrating the electrode system. Van Uitert and Haas (*loc. cit.*) have shown, by using a cell consisting of a hydrogen electrode and a silver–silver

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* Part I, *J.*, 1955, 1175.

chloride electrode, that the glass–calomel cell used in titrations measures hydrogen-ion activity as defined by a hydrogen electrode, an empirical calibration for one pH being valid over a wide range of hydrogen-ion concentrations under the same conditions of solvent mixture and ionic concentration. We have confirmed this.

If $(a_{\mathrm{H}^+})_0$ is the hydrogen-ion activity given by the pH meter reading, and $(c_{\mathrm{H}^+})_c$ is the stoicheiometric concentration assuming complete dissociation, we have found that

$$(a_{\mathrm{H}^+})_0/\gamma_{\mathrm{H}^+}(c_{\mathrm{H}^+})_c = k = 1{\cdot}56 \pm 0{\cdot}03 \quad . \; . \; . \; . \; . \quad (1)$$

for our electrode system under the conditions of our titrations, and over a range of pH values. The values for γ were obtained by interpolation from Harned and Owen's data (*loc. cit.*).

As has been previously pointed out, the other terms in the equations used for calculating $\bar{n}$ and $[\mathrm{L}^-]$ are in molarities. The hydrogen-ion term may be expressed similarly. From (1)

$$\gamma_{\mathrm{H}^+}(c_{\mathrm{H}^+})_c = (a_{\mathrm{H}^+})_0/1{\cdot}56$$

$$\therefore \quad (c_{\mathrm{H}^+})_c = (a_{\mathrm{H}^+})_0/k'$$

$$\therefore \quad \mathrm{pH}_c = \mathrm{pH}_0 + k''$$

In the present work, $k'' = 0{\cdot}07$. This is clearly the correction to be added to the pH meter reading.

Following Irving and Rossotti's nomenclature (*J.*, **1954**, 2907), the stability constants obtained by using this correction are termed " practical " constants.

EXPERIMENTAL AND RESULTS

Dioxan (B.D.H., " AnalaR " grade) was purified according to Weissberger and Proskauer (" Organic Solvents," Oxford Univ. Press, 1935).

The rest of the materials used were as in Part I (*loc. cit.*) and the potentiometric titrations were carried out as described there, except that the titrated solution contained 50% (v/v) of dioxan.

Results.—Non-thermodynamic ionisation exponents for the acids are given in Table 1. Previously, for work in aqueous solution, the first ionisation exponents were obtained spectrophotometrically; in 50% dioxan–water this was no longer convenient, so approximate figures obtained by potentiometric titration were used and are quoted in Table 1. Although their use might in some cases cause slight error in the lower $\bar{n}$ values, the general conclusions reached are in no way invalidated.

TABLE 1.

Acid	First iontn. exponent	Second iontn. exponent
Quinoline-8-carboxylic	<2	7·76
Quinoline-2-carboxylic	1·8	5·39
*iso*Quinoline-1-carboxylic	not detd.	5·46
Picolinic	~1·5	5·71
6-Methylpicolinic	<1	6·59

Stability data for chelated complexes. Titration figures are given for complexes between copper and quinoline-8-carboxylic acid as an example in Table 2, so that the pH range over which chelation takes place in dioxan–water may be compared with that given for water in Part I. It will be seen that once again complex formation takes place at low pH's, with the attendant difficulties discussed previously. Nevertheless stability constants have again been

TABLE 2.

Quinoline-8-carboxylic acid (0·0230 g.). Concn. of $\mathrm{HClO_4}$: 0·0866N, concn. of NaOH: 0·1034N. Initial vol.: 68·4 ml.

NaOH, ml.	3·385	3·853	4·091	4·392	4·610	4·778	4·847	4·922	5·022	5·110
pH	2·89	3·04	3·15	3·35	3·55	3·74	3·84	3·98	4·20	4·47
$\bar{n}$	0·34	0·58	0·67	0·84	0·97	1·13	1·18	1·24	1·35	1·44
log 1/[L⁻]	7·80	7·76	7·63	7·48	7·32	7·19	7·12	7·01	6·83	6·79

taken as the values of log $1/[L^-]$ at $\bar{n} = \frac{1}{2}$, 1, and $1\frac{1}{2}$. In a number of cases constants have also been evaluated by the method of least squares as suggested by Irving and Rossotti (*J.*, 1953, 3397); the maximum difference between the two figures is less than 0·2, and in view of what was said in Part I concerning the accuracy of the results it has not been thought necessary to quote these constants.

For complexes other than that formed by copper and quinoline-8-carboxylic acid, only stability constants are quoted; these are given in Table 3. Figures in parentheses have been obtained from the equation log K_1 + log K_2 = log K_s, or occasionally by slight graphical extrapolation.

TABLE 3.

Metal	log K_1	log K_2	log K_s	Metal	log K_1	log K_2	log K_s
Quinoline-8-carboxylic acid				Picolinic acid			
Cu	7·8	—	14·7	Cu	—	6·6	—
Ni	6·2	5·2	11·4	Ni	(6·1)	6·1	12·2
Co	5·3	4·3	9·6	Co	(5·9)	5·4	11·3
Zn	4·9	(4·1)	9·0				
Pb	4·5	—	—	6-Methylpicolinic acid			
Mn	4·2	—	—	Cu	—	~8	—
				Ni	(7·4)	5·8	13·2
Quinoline-2-carboxylic acid				Co	(6·6)	5·6	12·1
Ni	5·3	5·0	10·4				
Co	5·3	4·8	10·2				
Zn	5·1	4·6	9·7				

*iso*Quinoline-1-carboxylic acid gave derivatives too insoluble for stability constants to be determined. With quinoline-2-carboxylic acid and copper a precipitate appeared at too low a pH for values to be obtained.

DISCUSSION

The first ionisation exponents of the parent acids are in the order quinoline-8-carboxylic = quinoline-2-carboxylic > picolinic > 6-methylpicolinic acid; and the second ionisation exponents in the order quinoline-8-carboxylic > 6-methylpicolinic > picolinic > quinoline-2-carboxylic acid. These, as expected, are the same as in aqueous solution. Hence the complexes formed by quinoline-8-carboxylic acid should be by far the most stable. This is not so, and both increased ring size and steric factors are probably effective in the reduction of stability, the first as may be seen by the fact that log K_1 is considerably lower than expected for both nickel and cobalt when compared with the corresponding values using picolinic acid, and the second because the spreading factor is very much smaller with this latter acid.

In the case of 6-methylpicolinic acid the spreading factor leaves no doubt of steric hindrance although, with both nickel and cobalt, log K_1 is greater than it is when picolinic acid is the chelating agent; the latter fact is not unexpected when second dissociation exponents are compared.

With quinoline-2-carboxylic acid the effect of the second dissociation exponent would be to make the complexes less stable than those of picolinic acid; in addition, steric hindrance due to the benzenoid ring might be expected although this is not obvious from the spreading factor. In fact, examination of models or the construction of scale diagrams shows the 6-methyl group to have a much greater steric effect than the 5 : 6-benzenoid ring so that the much lower spread with quinoline-2-carboxylic acid is not surprising.

It is not always possible, however, to rely on deductions made from the magnitude of the spreading factor. With the compounds we have studied it would be expected that the factor would be less for cobalt complexes, having tetrahedral configuration, than for nickel and copper compounds with a planar structure, the latter especially. Insufficient figures are given for copper compounds but the expectation is not borne out on comparing the nickel and cobalt derivatives. Neither is it in other cases quoted in the literature as may be seen, for example, in the figures for " oxine " complexes and related compounds given by Irving and Rossotti (*J.*, 1954, 2910) and in those of Freiser quoted in the same paper. It is possible, of course, that the nickel is tetrahedrally bonded, although it is not probable that such would be the case with copper.

One point which emerges from the figures is that behaviours in water and dioxan–water are not exactly parallel; in particular, the values of log K_1 and log K_2 for the nickel and cobalt complexes are greater for picolinic than for 6-methylpicolinic acid in water, although this order is reversed in dioxan–water for log K_1 but not for log K_2. This behaviour is not unexpected in view of the comparatively large increase in the second dissociation exponent for 6-methylpicolinic acid in dioxan–water, but it does serve to underline Irving's warning (*Analyst*, 1952, **77**, 841) that it may not be possible always to correlate conclusions drawn from experiments in different media, or to assume that findings in one solvent are always true for another.

It may be noted that with each acid the stabilities of the chelated compounds studied follow the Irving–Williams order.

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