

## Metal Ammine Formation in Solution

### XIII. The Copper(II)-Pyridine System

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Some authors have interpreted their results from pH and other 'ligand' methods to mean that coordination number of the copper(II) ion in aqueous pyridine exceeds 4. However, the present investigation has shown that this is not the case; the high values for the formation function  $\bar{n}$ , were found previously because the authors had not considered the fact that pyridinated ions as well as pyridine itself have a strong 'salting-in' effect on pyridine. In this paper the salting-in effect of pyridine is examined by vapour pressure and by glass electrode measurements of pyridinium salt solutions. The copper(II)-pyridine formation curve was determined in 0.5 M pyridinium nitrate both by glass electrode and optical methods, the latter using the principle of corresponding solutions. The two kinds of measurements were in good agreement after the necessary corrections for the salting-in effect of pyridine and, especially, the pyridinated complexes had been made. Finally the spectra of the four copper(II)-pyridine complexes were resolved from the mixed spectra, and the influences on the spectrum of chloride ions and the high pyridine concentrations were examined. There was no spectral evidence for the existence of complexes with more than four pyridine molecules, but evidence was found for ion-pair association and for the formation of the dichlorodipyridine complex in pure pyridine.

Most authors<sup>1-7</sup> have assumed that the tetrapyridine-copper(II) ion is the highest complex formed in aqueous copper(II)-pyridine solutions. However, other authors believe that higher ammine complexes are formed. Thus Mellor and Maley<sup>8</sup> assumed that the copper(II) ion is present in a pyridine solution as the hexapyridine complex in agreement with the existence of pyridinated copper(II) salts with up to 6 moles of pyridine per copper atom.<sup>9,10</sup> Russell, Cooper and Vosburgh<sup>11</sup> measured the paramagnetism of copper(II) amines in solution, and presented some evidence to show that the pentapyridine complex should be more stable than the penta-ammonia complex. This seems to be consistent with recent results of Leussing and Hansen.<sup>12</sup> These authors found from glass electrode measurements and distribution experiments with toluene that the formation curve at relatively low pyridine concentrations

continued beyond  $\bar{n} = 4$  and gave the following values for the consecutive constants in 1 M  $\text{KNO}_3$  at  $25^\circ\text{C}$ :  $\log K_1 = 2.59$ ,  $\log K_2 = 1.74$ ,  $\log K_3 = 1.60$ ,  $\log K_4 = 0.61$ , and  $\log K_5 = 0.49$ . Leussing and Hansen<sup>12</sup> claimed support for their conclusions by comparing their results with those for the copper(II)-dipyridyl system, which, according to many investigators,<sup>13</sup> behaves as a chelate system with the characteristic coordination number 6. However, Leussing and a coworker<sup>14</sup> have expressed themselves more cautiously in a following paper, in which they found that the uptake of the fifth pyridine was endothermic. Thus they considered the possibility that 'the fifth pyridine molecule is not really coordinated in the true sense of the word but merely finds greater freedom in the region of solvent surrounding the tetrammine'. They continued: 'This region may provide better solvent properties for an unassociated pyridine molecule than the highly hydrogen bonded region in the bulk of the solvent'. The author agrees with this point of view. The present paper, which utilizes old unpublished measurements, has been written in order to show that the reason why Leussing and coworkers as well as other authors<sup>3,6,7</sup> have found values of the formation function that are too high for  $\bar{n} > 2$  is that they have not considered the fact that not only pyridine itself but also pyridinated ions have a strong salting-in effect on pyridine.

#### THE ACTIVITY COEFFICIENT OF PYRIDINE FROM VAPOUR PRESSURE MEASUREMENTS

The vapour pressure of pyridine was measured using a well-known method in which a known volume of an inert gas was bubbled slowly through the solution, the pyridine thus removed being titrated after absorption in acid. The method was similar to that used previously by the author<sup>15</sup> (for further details, see Experimental). The data for these experiments are given in Table 1. The pyridine concentration,  $C_{\text{py}}(\text{av.})$ , is the average molar concentration during an experiment. The pyridine vapour pressure,  $p_{\text{py}}$  (in mm of Hg), was calculated from the corrected volume of gas, vol, which has been passed through the solution and the required amount of titrated NaOH. The data in the table show that the determined pyridine vapour pressure is independent of the rate

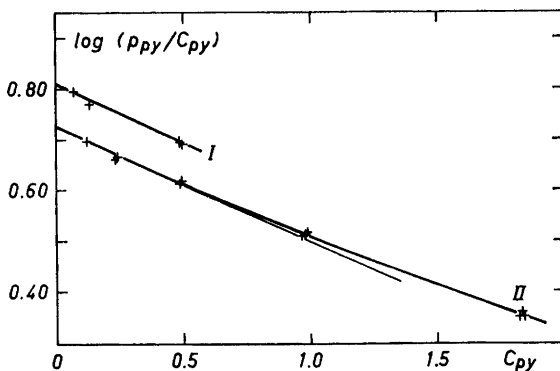


Fig. 1.  $\log p_{\text{py}}/C_{\text{py}}$  versus  $C_{\text{py}}$ . I, water ( $C_{\text{salt}} = 0$ ), II, 0.5 M  $\text{pyHNO}_3$ ,  $25^\circ\text{C}$ .

of gas bubbling (4th column of the table) and, therefore, must be assumed to be the equilibrium value.

A plot of  $\log(p_{\text{py}}/C_{\text{py}})$  versus  $C_{\text{py}}$  both for pure water as solvent and for 0.5 M pyHNO<sub>3</sub> gave straight lines with the same slope within the uncertainty of the measurements (see Fig. 1). From the intersection of the lines with the ordinate, limiting values of  $\log(p_{\text{py}}/C_{\text{py}})$  for  $C_{\text{py}} = 0$  were obtained. From the limiting value in pure water 0.806, the activity coefficient of pyridine,  $f_{\text{py}}$ , was calculated using the relationship

$$f_{\text{py}} = \left( \frac{p_{\text{py}}}{C_{\text{py}}} \right) / \left( \frac{p_{\text{py}}}{C_{\text{py}}} \right)_{C_{\text{py}}=0} \quad \text{or} \quad \log f_{\text{py}} = \log \frac{p_{\text{py}}}{C_{\text{py}}} - 0.806$$

and is given in the penultimate column of Table 1.

Many authors<sup>16</sup> have found that the solubility of neutral molecules in salt solutions approximately follows Setschenow's rule. For pyridine this can be expressed as

$$\log f_{\text{py}} = a C_{\text{salt}}$$

Table 1. The pyridine vapour pressure measurements at 25°C.

No.	$C_{\text{py}}(\text{av.})$	vol.	$\frac{\text{liter}}{\text{hour}}$	ml NaOH 0.930 M	$p_{\text{py}}$ (mm Hg)	$\log \frac{p_{\text{py}}}{C_{\text{py}}}$	$f_{\text{py}}(\text{found})$	$f_{\text{py}}(\text{calc.})$
In water ( $C_{\text{salt}} = 0$ ): $\log f_{\text{py}}(\text{calc.}) = -0.235C_{\text{py}} + 0.017C_{\text{py}}^2$ .								
1	0.498	7.635	2.90	1.082	2.452	0.692	0.770	0.770
2	0.4875	7.181	1.44	1.003	2.416	0.695	0.775	0.776
3	0.1308	11.86	2.24	0.5214	0.7606	0.765	0.910	0.931
4	0.1308	11.13	1.51	0.500	0.7772	0.774	0.930	0.931
5	0.06905	12.855	1.72	0.3214	0.4325	0.794	0.980	0.963
6	0.06905	25.065	1.49	0.6244	0.4310	0.795	0.975	0.963
	0				extrapol.	0.806	1	1
In 0.5 M pyHNO <sub>3</sub> : $\log f_{\text{py}}(\text{calc.}) = -0.235C_{\text{py}} + 0.017C_{\text{py}}^2 - 0.16C_{\text{pyHNO}_3}$								
7	1.849	3.535	1.96	0.857	4.194	0.356	0.295	0.291
8	1.840	4.604	1.71	1.135	4.264	0.365	0.301	0.292
9	1.830	3.720	1.84	0.894	4.158	0.356	0.295	0.293
10	0.989	5.312	1.84	1.002	3.263	0.518	0.428	0.422
11	0.979	5.923	3.74	1.097	3.204	0.515	0.425	0.423
12	0.969	5.390	1.47	0.982	3.152	0.512	0.423	0.425
13	0.4962	7.116	1.76	0.848	2.062	0.619	0.540	0.535
14	0.4871	8.896	1.79	1.032	2.007	0.615	0.535	0.537
15	0.2402	8.605	1.70	0.552	1.110	0.665	0.601	0.609
16	0.2353	7.210	2.09	0.451	1.082	0.663	0.598	0.610
17	0.1238	8.826	2.26	0.3153	0.618	0.698	0.649	0.647
18	0.1207	9.242	1.94	0.3216	0.602	0.698	0.649	0.648
19	0.1172	12.185	2.00	0.408	0.5793	0.694	0.643	0.650
	0				extrapol.	0.726	0.692	0.692
In 0.5 M KCl: $\log f_{\text{py}}(\text{calc.}) = -0.235C_{\text{py}} + 0.017C_{\text{py}}^2 + 0.064C_{\text{KCl}}$								
20	0.4839	4.556	1.07	0.678	2.575	0.726	0.832	0.836
21	0.4766	5.580	1.55	0.825	2.557	0.730	0.839	0.837
	0							1.116

where  $\alpha$ , the salting-out coefficient, is a constant. However, it is noteworthy that the influence of pyridine itself on  $f_{\text{py}}$  can be expressed by the same rule. This is shown in Table 1 where the data are summarized in such formulae, and it will be seen that the values of the activity coefficient calculated from them ( $f_{\text{py}}(\text{calc.})$ ) reproduce the measurements very well. The formulae given show directly that while pyridine is salted-in by pyridine and by pyridinium nitrate, it is salted-out by potassium chloride. The positive quadratic term in the expression for the dependence of the pyridine concentration is only of minor importance if  $C_{\text{py}} < 1 \text{ M}$ , but extends the usefulness of the formula until very high pyridine concentrations. From the measured vapour pressure of pure pyridine, 21 mm of Hg at 20°,<sup>17</sup> and the boiling point 115.3°, the vapour pressure at 25° was estimated to be 25.4 mm of Hg. Using this value for pure pyridine, which is 12.4 M,  $\log f_{\text{py}}$  in this solvent was calculated to be  $-0.49$  compared with  $-0.30$  from the formula:

$$\log f_{\text{py}} = -0.235 C_{\text{py}} + 0.17 C_{\text{py}}^2$$

However, the influence of the quadratic term is in this case so high that a reduction of less than 10 % in this term would give complete agreement.

#### THE ACTIVITY EFFECTS OF PYRIDINE AND VARIOUS SALTS FROM GLASS ELECTRODE MEASUREMENTS

Table 2 gives some values of the acid dissociation constant of pyridine

$$K_a = [\text{H}^+][\text{py}]/[\text{pyH}^+]$$

in 0.5 M and 1 M pyridinium nitrate at 25°C. These were determined by a potentiometric method based on the difference in the glass electrode potentials ( $E_{\text{I}} - E_{\text{II}}$ ) between nitric acid solutions (I) and pyridine solutions (II) in the same salt medium. Calculations were made according to the equation<sup>18</sup>

$$pK_a = 0.4343 (F/RT) (E_{\text{I}} - E_{\text{II}}) + \log C_{\text{pyHNO}_3} - \log[\text{H}^+] - \log[\text{py}]$$

where  $[\text{H}^+]$  and  $[\text{py}]$  are the actual concentrations of hydrogen ion and pyridine in solutions I and II, respectively. These concentrations are close to the total or formal concentrations of the added substances, but are corrected for self-dissociation of the pyridinium salt, and for non-equivalence of acid and base in the added pyridinium nitrate (see Experimental). The added concentrations

Table 2. Some determinations of the acid dissociation constant of pyridine in pyridinium nitrate solutions at 25°C.

$C_{\text{pyHNO}_3}$	Sol. I, $[\text{H}^+]$	Sol. II, $[\text{py}]$	$E_{\text{I}} - E_{\text{II}}$	$pK_a$
0.500	0.01932	0.02068	0.1241	5.214
0.500	0.02130	0.04839	av. 0.1494	5.214
0.500	0.02301	0.04466	av. 0.1497	5.220
0.500	0.05271	0.04466	av. 0.1705	5.213
				av. 5.215
1.000	0.02600	0.04285	av. 0.1318	5.183

of nitric acid and pyridine are on the other hand so small ( $\leq 0.05$  M) that the acid dissociation constant determined can be taken as the true concentration constant for the medium in question. This constant is related to  $K_a^\circ$ , the activity constant by the expression,

$$pK_a = pK_a^\circ + \log (f_{H^+}f_{py}/f_{pyH^+})$$

From the data in Table 2 and the general expression,

$$pK_a = pK_a^\circ + \alpha C_{BH^+}$$

where  $\alpha$  is a constant and B is an uncharged base, the values,  $pK_a^\circ = 5.247$  and  $\log (f_{H^+}f_{py}/f_{pyH^+}) = -0.064 C_{pyHNO_3}$ , were obtained. From a comparison of this expression for the activity coefficient quotient with that for  $\log f_{py}$  in Table 1, it is obvious that  $f_{pyH^+}$  decreases essentially more than  $f_{H^+}$  with increasing concentration of pyridinium nitrate. Comparing, on the other hand, the present value of the  $pK_a^\circ$  with that of Bruehlmann and Verhoek<sup>3</sup> in 0.5 M  $KNO_3$  at 25° ( $pK_a = 5.45$ ), it can qualitatively be estimated that potassium nitrate has the opposite influence on the activity coefficients. Hawkins and Perrin<sup>6</sup> have found the  $pK_a$  in 0.15 M  $NaClO_4$  at 20° to be 5.32. If this value is converted to 25° using Berthelot's<sup>19</sup> value for the heat of neutralization of pyridine, 5.1 kcal, the value 5.26 is obtained in good agreement with the present value for  $pK_a^\circ = 5.247$ .

When studying by a ligand method such a relatively weak complex system as that of copper(II)-pyridine in a pyridinium salt medium, the values of  $C_L$  and  $C_M$  must be so high in order to use the expression,

$$\bar{n} = (C_L - [L])/C_M$$

that the activity coefficients cannot be assumed to be constant. To examine this

Table 3. Some determinations of the influence of pyridine and various salts on  $pK_a$  in 0.5 M  $pyHNO_3$  at 25°C.

$C_{pyHNO_3}$	$C_{KCl}$	$C_{BaCl_2}$	$C_{py}$	$\Delta pK_a$	$\Delta pK_a/\Delta C_X$	X
0.500			0.02–0.05	0		
0.500			0.396	–0.036	–0.091	py
0.500			0.777	–0.058	–0.075	py
0.500			1.875	–0.146	–0.078	py
0.500			2.33	–0.196	–0.084	py
					av. –0.082	
1.00			0.0429	–0.057	–0.115	$pyHNO_3$
0.500	0.200		0.0484	+ 0.027	0.14	KCl
0.500	0.200		0.777	–0.018	0.20	KCl
					av. + 0.16	
0.500		0.100	0.0484	+ 0.012	0.12	$BaCl_2$
0.500		0.200	0.0484	+ 0.028	0.14	$BaCl_2$
0.500		0.200	0.777	–0.024	0.17	$BaCl_2$
0.500		0.400	1.875	–1.07	0.10	$BaCl_2$
					av. + 0.14	

point further, the author has measured with a glass electrode the potential difference between some 0.5 M pyridinium nitrate solutions with high pyridine concentrations and (or) with added neutral salts, and reference solutions in 0.5 M  $\text{pyHNO}_3$  with a low concentration of pyridine (0.02–0.05 M). Similar measurements have been performed previously by the author<sup>18</sup> with some ammonia systems. However, in the present case the data have been treated in a modified way. The measured potential difference permits the direct calculation of an apparent pyridine activity,  $a'_{\text{py}}$ , in the solution. Introducing the pyridine (and pyridinium) concentration this can be expressed as an apparent increase in  $\text{p}K_a$  (denoted  $\Delta' \text{p}K_a$  in Table 3). The data collected in Table 3 show that the influences of pyridine and the added salts on  $\text{p}K_a$  seem to be additive, and for each substance approximately proportional to its concentration as can be seen from the fair constancy of  $\Delta' \text{p}K_a / \Delta C_x$  in the penultimate column of the table. The influences of the various substances are qualitatively the same as those on  $\log f_{\text{py}}$ : pyridine and pyridinium salt have a decreasing influence, and salts such as potassium chloride an increasing influence.

The activity function  $\Delta' \text{p}K_a$  in the solutions for which  $C_{\text{pyHNO}_3} = 0.50$  M is related to  $a'_{\text{py}}$  by the expression,

$$\Delta' \text{p}K_a = \log a'_{\text{py}} - \log [\text{py}] \quad (1)$$

The physical meaning of  $\Delta' \text{p}K_a$ , in the following denoted  $\log F$ , is very complex,<sup>20</sup> but if the simplifying assumption is made that the electricity in the cells alone is transported by pyridinium and nitrate ions, calculation shows that  $F$  should be identical with the variation in  $f_{\text{py}} / (f_{\text{pyH}} + f_{\text{NO}_3^-})^t$ , where  $t \sim 0.60$  is the transference number of the nitrate ion in pyridinium nitrate solutions.<sup>21</sup>

#### THE FORMATION CURVE OF THE COPPER(II)-PYRIDINE SYSTEM FROM GLASS ELECTRODE MEASUREMENTS

The data from the copper(II)-pyridine investigations are collected in Table 4. The calculations were based on the potential differences as measured by glass electrodes between copper(II)-pyridine-0.5 M  $\text{pyHNO}_3$  solutions and a standard 0.0485 M pyridine-0.5 M  $\text{pyHNO}_3$  solution. The apparent pyridine activity,  $a'_{\text{py}}$ , was directly calculated from the measured potential difference,  $E - E_{\text{st}}$ , according to the expression,

$$-\log a'_{\text{py}} = (E - E_{\text{st}}) / 0.0591 - \log [\text{py}]_{\text{st}}$$

For small pyridine concentrations (solutions 1–10)  $a'_{\text{py}}$  was identified with  $[\text{py}]$ , and  $\bar{n}$  calculated from the expression:

$$\bar{n} = (C_{\text{py}} + [\text{H}^+] - [\text{py}]) / C_{\text{Cu}} \quad (2)$$

For higher pyridine and copper concentrations, it is necessary to calculate the free pyridine concentration from the expression,

$$[\text{py}] = a'_{\text{py}} / F$$

where  $F$  according to the results in the preceding section, is given by an equation,

$$\log F = -0.082 [\text{py}] + \alpha C_{\text{Cu}}$$

Table 4. Glass electrode measurements of copper(II)-pyridine solutions in 0.5 M pyHNO<sub>3</sub> at 25°C.

No.	$C_{\text{Cu}(\text{NO}_3)_2}$	$C_{\text{py}}$	$-\log[\text{py}]$	$[\text{py}]$	$[\text{H}^+]$	$\bar{n}$	$-\log[\text{py}]_{\text{st}} = 1.315$	
1	0.04052	0.01076	2.904	0.00125	0.00244	0.295		
2	0.1020	0.04833	2.674	0.00212	0.00144	0.467		
3	0.03034	0.01862	2.537	0.00290	0.00105	0.553		
4	0.04052	0.03842	2.296	0.00505	0.00060	0.838		
5	0.01013	0.01467	2.229	0.00590	0.00052	0.917		
6	0.1020	0.1476	1.948	0.01128	0.00027	1.339		
7	0.04052	0.07047	1.878	0.01323	0.00023	1.418		
8	0.04052	0.1178	1.474	0.0336	0.00009	2.080		
9	0.1020	0.2476	1.493	0.0322	0.00009	2.113		
10	0.04052	0.1418	1.329	0.0469	0.00007	2.344		
			Calc. with $\log F = -0.082[\text{py}] - 0.40 C_{\text{Cu}(\text{NO}_3)_2}$					
No.	$C_{\text{Cu}(\text{NO}_3)_2}$	$C_{\text{py}}$	$-\log a'_{\text{py}}$	$a'_{\text{py}}$	$\bar{n}'$	$-\log[\text{py}]$	$[\text{py}]$	$\bar{n}$
11	0.04052	0.1775	1.156	0.0698	2.63	1.134	0.0735	2.57
12	0.1020	0.414	0.975	0.1060	3.02	0.924	0.119	2.89
13	0.1020	0.495	0.824	0.1492	3.39	0.769	0.170	3.19
14	0.04052	0.3176	0.755	0.1760	3.49	0.723	0.1890	3.17
15	0.1020	0.667	0.572	0.2680	3.91	0.505	0.312	3.48
16	0.1020	0.789	0.437	0.366	4.15	0.360	0.436	3.46
17	0.1020	0.982	0.303	0.498	4.745	0.212	0.613	3.62
18	0.2028	1.551	0.259	0.551	4.93	0.115	0.767	3.87
19	0.3253	2.995	0.036	0.920	6.38	-0.253	1.79	3.71
20	0.4066	3.752	0.002	0.995	6.78	-0.341	2.19	3.84

The salting-out coefficient of the pyridine complexes,  $\alpha$ , must be assumed to have a relatively high negative value. This value could only be determined from the measurements under certain assumptions.

From Fig. 3 A, it is obvious that the absorption curves of dilute copper(II) nitrate solutions in 0.5 M pyHNO<sub>3</sub> are displaced regularly towards the blue with increasing pyridine concentration, while, at the same time, the absorption is found to increase. A limiting curve seems to have been reached in about 2 M pyridine solution. However, on increasing the pyridine concentration to 7 M, a slight lowering of the band was observed (*cf.* Fig. 2, in Ref.<sup>4</sup>). As  $\lambda_{\text{max}}$  remained practically unchanged, this observation can hardly be interpreted as a pentammine effect, but could be explained by ion-pair formation between the pyridinated copper(II) ion and the nitrate ion.<sup>22</sup> It is, therefore, most probable that the formation of the tetrapyridine complex is first completed at pyridine concentrations a little higher than 2 M. Under this assumption,  $\alpha$  was determined by trial and error to be  $-0.40$ . This value may be considered as an average value for the salting-out coefficient of  $\text{Cu py}_n^{2+}$  for values of  $\bar{n}$  between 3 and 4.

The corrected values of  $\bar{n}$  are given in the lower part of Table 4. For comparison,  $\bar{n}'$  calculated in the usual way by identifying  $a'_{\text{py}}$  with  $[\text{py}]$  is given in the 6th column of the table. The data given show clearly how dominating the correction becomes with increasing pyridine and copper concentration;

for solutions 19 and 20  $\bar{n}'$  is seen to be even higher than 6 (compare Cabani<sup>23</sup>). Both sets of  $\bar{n}$ -values are plotted *versus*  $-\log [\text{py}]$  in Fig. 2. The corrected points (+) give a much more probable curve than the completely anomalous curve through the uncorrected points ( $\square$ ).

#### SPECTROPHOTOMETRIC DETERMINATION OF THE FORMATION CURVE

In order to obtain independent confirmation for the above theory, the formation curves were also determined spectrophotometrically by means of the principle of corresponding solutions.<sup>24</sup> The concentrations of copper(II) and pyridine in two corresponding solutions,  $C_{\text{Cu}}$ ,  $C_{\text{py}}$ ,  $[\text{py}]$  and  $C_{\text{Cu}}^\circ$ ,  $C_{\text{py}}^\circ$ ,  $[\text{py}]^\circ$ , are related by

$$\bar{n} = \frac{C_{\text{py}} - [\text{py}]}{C_{\text{Cu}}} = \frac{C_{\text{py}}^\circ - [\text{py}]^\circ}{C_{\text{Cu}}^\circ} \quad (3)$$

Corresponding solutions have, by definition, the same distribution of complexes and, therefore, should also have the same concentration of free ligand, *i.e.*  $[\text{py}]^\circ = [\text{py}]$ . In the copper(II)-pyridine system examined, this can only be fulfilled for a limited range of concentrations. Further, when it was necessary to correct for salt effects, it was assumed that the apparent pyridine activities,  $a'_{\text{py}}$  as measured by the glass electrode, had the same value for corresponding solutions. From this assumption, the relationship,

$$[\text{py}]^\circ = (F/F^\circ) [\text{py}]$$

was obtained. From the equations,

$$\log F = -0.082[\text{py}] - 0.40 C_{\text{Cu}}$$

and

$$h = F/F^\circ$$

the expression

$$\log h = -0.40(C_{\text{Cu}} - C_{\text{Cu}}^\circ) \quad (4)$$

was obtained with the approximation that the pyridine concentration term is insignificant compared to the copper term. By inserting  $[\text{py}]^\circ = h[\text{py}]$  into (3) and solving the equations with respect to  $\bar{n}$  and  $[\text{py}]$  the following identities were determined

$$\bar{n} = \frac{C_{\text{py}}^\circ - hC_{\text{py}}}{C_{\text{Cu}}^\circ - hC_{\text{Cu}}} \quad (5)$$

$$[\text{py}] = \frac{C_{\text{Cu}}^\circ C_{\text{py}} - C_{\text{Cu}} C_{\text{Cu}}^\circ}{C_{\text{Cu}}^\circ - hC_{\text{Cu}}} \quad (6)$$

At low pyridine concentrations, the salt corrections are insignificant and thus, without introducing any great error, the assumption,  $h = 1$ , can be made. However, in this range of concentrations it is necessary to introduce another correction. From a comparison of the expressions (2) and (3), it is obvious that what is determined is not  $[\text{py}]$ , but more correctly  $[\text{py}] - [\text{H}^+]$ . For the 0.5 M  $\text{pyHNO}_3$  medium, therefore, eqn. (6) has the form,

$$[\text{py}] - \frac{0.5K_a}{[\text{py}]} = \frac{C_{\text{Cu}}^\circ C_{\text{py}} - C_{\text{Cu}} C_{\text{py}}^\circ}{C_{\text{Cu}}^\circ - C_{\text{Cu}}} \quad (7)$$



Table 5. Spectrophotometric measurements of copper(II)-pyridine solutions in 0.5 M pyHNO<sub>3</sub> at 23°C.

Nos. 1–5:  $C_{\text{Cu}} = 0.00505$  M. Corresponding solutions by means of  $\epsilon_{\lambda}$ ,  $C_{\text{py}}^{\circ}$ -adjustment curve with  $C_{\text{Cu}}^{\circ} = 0.03034$  M.  $[\text{H}^+]$  calc. with  $\text{p}K_{\text{a}} = 5.24$ .

No.	$C_{\text{py}}$	$\lambda(\text{m}\mu)$	$\epsilon_{\lambda}$	$C_{\text{py}}^{\circ}$	$C_{\text{py}}^{\circ}(\text{av.})$	$\bar{n}$	$[\text{py}] - [\text{H}^+]$	$[\text{py}]$	$-\log[\text{py}]$
1	0.00373	610	4.90	0.0195					
		590	3.32	0.0206	0.0198	0.635	0.00052	0.00198	2.703
		560	1.30	0.0195					
2	0.00471	610	5.01	0.0201					
		590	3.23	0.0202	0.0201	0.608	0.00163	0.00269	2.570
		560	1.35	0.0201					
3	0.00572	610	5.81	0.0230					
		590	3.75	0.0231	0.0230	0.683	0.00226	0.00316	2.500
		560	1.57	0.0230					
4	0.01065	610	9.18	0.0350					
		590	6.37	0.0350	0.0350	0.963	0.00578	0.00624	2.205
		560	3.01	0.0350					
5	0.01564	610	13.40	0.0485					
		590	9.74	0.0482	0.0484	1.295	0.00909	0.00939	2.027
		560	5.16	0.0485					

No. 6:  $C_{\text{Cu}} = 0.03034$  M,  $h = 1.02$ . Nos. 7–14:  $C_{\text{Cu}} = 0.1008$  M,  $h = 1.09$ .  $\epsilon_{\lambda}$ ,  $\log C_{\text{py}}^{\circ}$ -adjustment curve with  $C_{\text{Cu}}^{\circ} = 0.01008$  M.

No.	$C_{\text{py}}$	$\lambda(\text{m}\mu)$	$\epsilon_{\lambda}$	$2 + \log C_{\text{py}}^{\circ}$	$C_{\text{py}}^{\circ}(\text{av.})$	$\bar{n}'$	$-\log[\text{py}]'$	$\bar{n}$	$-\log[\text{py}]$
6	0.0723	610	20.97	0.573					
		590	16.3	0.575	0.0368	1.75	1.717	1.74	1.714
		560	9.15	0.550					
7	0.2536	610	29.54	0.750					
		590	24.45	0.760	0.0562	2.18	1.465	2.14	1.462
		560	14.42	0.740					
8	0.2957	610	36.15	0.890					
		590	30.77	0.886	0.0775	2.41	1.274	2.35	1.270
		560	20.38	0.895					
9	0.3797	610	46.45	1.113					
		590	41.8	1.105	0.1273	2.78	1.003	2.68	1.000
		560	29.43	1.096					
10	0.5005	610	56.4	1.350					
		590	53.1	1.343	0.2208	3.08	0.722	2.90	0.719
		560	40.85	1.340					
11	0.5853	610	59.2	1.439					
		590	57.5	1.450	0.2786	3.38	0.611	3.13	0.608
		560	45.25	1.446					
12	0.6152	610	60.2	1.470					
		590	58.1	1.466	0.2940	3.54	0.588	3.28	0.584
		560	45.9	1.470					
13	0.6922	610	63.0	1.572					
		590	62.1	1.580	0.3773	3.47	0.465	3.13	0.462
		560	50.0	1.580					
14	0.8670	610	66.35	1.740					
		590	65.9	1.715	0.5245	3.78	0.313	3.30	0.309
		560	53.85	1.705					

The data for these experiments are given in Table 5. Corresponding solutions were obtained as described in Ref.<sup>24</sup> by means of adjustment curves, which, for a chosen copper(II) concentration ( $C_{Cu}^{\circ}$ ), give the molar extinction coefficient,  $\epsilon_{\lambda}$ , as a function of the total concentration of pyridine ( $C_{py}^{\circ}$ ) at selected wavelengths. The extinction coefficients were measured at 610, 590, and 560  $m\mu$  and the values of  $C_{py}^{\circ}$  (or  $\log C_{py}^{\circ}$ ) for the solution in question are given in the 5th column of Table 5 for each of these wavelengths. These values which were obtained graphically, were found to be independent of the wavelength and their average is given in the 6th column of the table. In the following columns for solutions 1–5, values of  $\bar{n}$ ,  $[py]-[H^+]$  and  $[py]$ , calculated according to expressions (5) and (7) with  $h = 1$ , are given. For solutions 6–14 values calculated in the same way are denoted  $\bar{n}'$  and  $-\log[py]'$ . For these solutions corrected values of  $\bar{n}$  and  $-\log[py]$  calculated from eqns. (4), (5), and (6) are also given.

In Fig. 2 a comparison is made between the optical data and the glass electrode measurements. The optical method is at the limit of its applicability

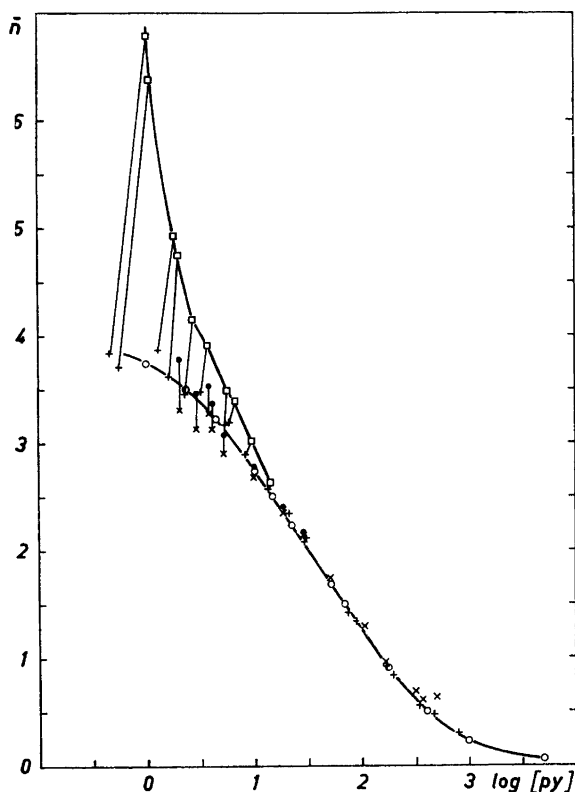


Fig. 2. The copper(II)-pyridine formation curve in 0.5 M  $pyHNO_3$ . From glass electrode measurements at 25° (uncorr.  $\square$ , corr.  $+$ ), optically by means of corresponding solutions at 23° (uncorr.  $\bullet$ , corr.  $\times$ ), and calculated at selected concentrations of pyridine by means of the derived constants at 25° and the  $F$ -function with  $C_{Cu} = 0$  (O-points)

for values of  $\bar{n} < 1$ . For this reason the  $\bar{n}$ -values in this range are too high.<sup>24</sup> The opposite is the case for values of  $\bar{n} > 3$ , where the corrected points seem to be too low. However, for the middle part of the curve the agreement between the two kinds of measurements is very satisfactory especially considering a small shift of the curve due to the different temperatures 23° and 25°.

#### ESTIMATION OF FORMATION CONSTANTS AND THE SPECTRA OF THE COPPER(II) PYRIDINE IONS

The formation constants were calculated from interpolated values of the ligand exponent for all half values of  $\bar{n}$  using the formation curve determined by glass electrode. The approximation of a set of preliminary constants was performed as previously described in detail.<sup>18</sup> The preliminary constants used were:

$$\log Q_n = -\log[\text{py}]_{\bar{n}=2} + \log \left( \frac{5-n}{n} x^{5-2n} \right)$$

where  $x = 1.346$  was derived from the midpoint slope. The temporary constants showed a good convergence, and after a few successive insertions, the values did not alter on repeating the procedure. The constants thus obtained, which are the same as those communicated in Ref.<sup>4</sup>, are given in Table 6 together with other relevant material. The values of  $\bar{n}$  in the last column were calculated by means of the constants for the given values of  $-\log a'_{\text{py}}$  (for  $C_{\text{Cu}} = 0$ ), and their identity with  $n - \frac{1}{2}$  shows the inner agreement of the data.

The spectra of the individual complexes were obtained by resolving the spectra of seven copper(II)-pyridine solutions with  $\bar{n}$  varying from 0.9 to 3.7 (see Table 7, and Fig. 3 A). The measurements were performed at 23°, and the composition of the solutions is given in the upper part of the table. The  $\log K_n$ -values at 23° were taken to be 0.02-unit higher than at 25°, the correction being estimated from the thermochemical measurements of Leussing and Gallagher.<sup>12</sup> The concentrations of free pyridine,  $[\text{H}^+]$ , and  $\bar{n}$  were approximated from the formal concentrations of copper(II) and pyridine by means of the formation curve. Afterwards  $\alpha_n = [\text{Cu py}_n^{2+}]/C_{\text{Cu}}$  and  $\bar{n}$  were computed from  $a'_{\text{py}}$  (with  $C_{\text{Cu}} = 0$ ) to provide an internal check on the calculation.

The extinction coefficients of the pure species,  $\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$ , and  $\epsilon_4$ , were estimated by solving at each wavelength seven equations of the form

$$\sum_1^4 \alpha_n \epsilon_n = \epsilon_{\bar{n}} - \alpha_0 \epsilon_0$$

Table 6. The copper(II)-pyridine formation constants in 0.5 M pyridinium nitrate at 25 C.

$n$	$\bar{n} = n - \frac{1}{2}$	$-\log[\text{py}]$	$-\log a'_{\text{py}}$	$\log Q_n$	$\log K_n$	$\bar{n}$ (calc.)
1	0.5	2.61	2.61	2.50	2.408	0.500
2	1.5	1.84	1.84	1.815	1.880	1.500
3	2.5	1.17	1.176	1.205	1.137	2.500
4	3.5	0.37	0.405	0.52	0.605	3.500
				$\log \beta_4$	6.03	

Table 7. Analysis of absorption spectra of copper(II)-pyridine solutions in 0.5 M pyHNO<sub>3</sub> at 23°C.

Composition of solutions calculated with: log $K_1 = 2.428$ , log $K_2 = 1.900$ , log $K_3 = 1.157$ , log $K_4 = 0.625$ . $\bar{n} = 0$ , $C_{\text{Cu}(\text{NO}_3)_2}$ 0.03 to 0.1 M, $C_{\text{HNO}_3} = 0.05$ M.									
$\bar{n}$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$-\log a'_{\text{py}} - \log[\text{py}]$		$C_{\text{py}}$	$C_{\text{Cu}}$
0.906	0.323	0.464	0.198	0.015	0	2.271	2.271	0.03231	0.03034
1.684	0.067	0.326	0.473	0.124	0.010	1.738	1.737	0.03515	0.01008
2.235	0.013	0.145	0.490	0.299	0.053	1.372	1.368	0.06528	0.01008
2.745	0.002	0.045	0.334	0.445	0.174	1.032	1.024	0.1225	0.01008
3.227	0	0.009	0.149	0.448	0.394	0.680	0.662	0.2504	0.01008
3.547	0	0.002	0.055	0.337	0.606	0.370	0.332	0.5023	0.01008
3.736	0	0	0.020	0.224	0.756	0.096	0.017	1.000	0.01008

Molar extinction coefficients  $\epsilon_n^-$  found and calculated.

$n$		690	670	650	630	610	590	560	530	510 m $\mu$
0.906	f.	17.54	15.97	13.89	11.15	8.23	5.65	2.60	0.93	0.47
	calc.	17.58	16.00	13.73	11.11	8.23	5.67	2.71	0.90	0.53
1.684	f.	29.3	28.45	26.5	24.0	19.47	15.00	8.82	3.67	2.11
	calc.	29.07	28.44	26.72	24.13	19.64	15.13	8.60	3.73	2.10
2.235	f.	37.6	37.8	37.35	35.98	32.55	27.07	17.02	8.47	4.52
	calc.	37.83	37.98	37.46	36.02	32.08	26.87	17.20	8.30	4.48
2.745	f.	44.3	45.5	46.8	47.45	45.2	41.0	29.25	15.10	8.35
	calc.	44.27	45.28	46.50	47.22	45.69	41.13	29.23	15.42	8.37
3.227	f.	46.9	49.0	52.1	55.9	58.0	55.5	43.3	24.9	13.74
	calc.	46.86	49.05	52.52	56.15	58.20	55.69	43.30	24.68	13.84
3.547	f.	45.7	49.2	55.0	60.6	65.7	65.6	53.8	32.4	18.7
	calc.	45.84	49.35	54.64	60.66	65.56	65.23	53.66	32.13	18.49
3.736	f.	44.3	48.8	55.0	62.8	69.5	70.5	60.1	36.7	21.5
	calc.	44.25	48.66	55.14	62.72	69.43	70.68	60.16	36.97	21.62

Estimated molar extinction coefficients  $\epsilon_n$  of the individual Cu py<sub>*n*</sub><sup>2+</sup>.

$n=0$	5.75	4.40	3.28	2.16	1.29	0.72	0.27	0.10	0.05
1	18.38	15.62	12.10	8.61	6.32	4.06	1.66	0.17	0.0
2	32.0	32.7	31.22	27.95	20.26	14.10	6.84	2.84	2.06
3	57.7	57.43	58.4	58.93	57.8	50.92	33.17	15.16	6.91
4	40.6	46.5	54.8	64.76	74.2	78.03	69.57	44.33	26.5

The calculation was made by the method of least squares, and the computed molar extinction coefficients of the four complexes at nine wavelengths are given at the bottom of Table 7 together with the directly determined extinction coefficient,  $\epsilon_0$ , of the aquo copper(II) ion. The absorption curves of the pure species are shown in Fig. 3 A, and have, as one should expect, a lower halfwidth than the equilibrium solutions. In the middle part of Table 7, the experimentally determined mean extinction coefficients,  $\epsilon_{\bar{n}}$ , of the equilibrium solutions are compared with those calculated from the extinction coefficients of the pure species. The agreement is excellent.

As expected, the absorption spectra of dilute copper(II) nitrate and copper(II) chloride in 1 M pyridine are practically identical. However, this

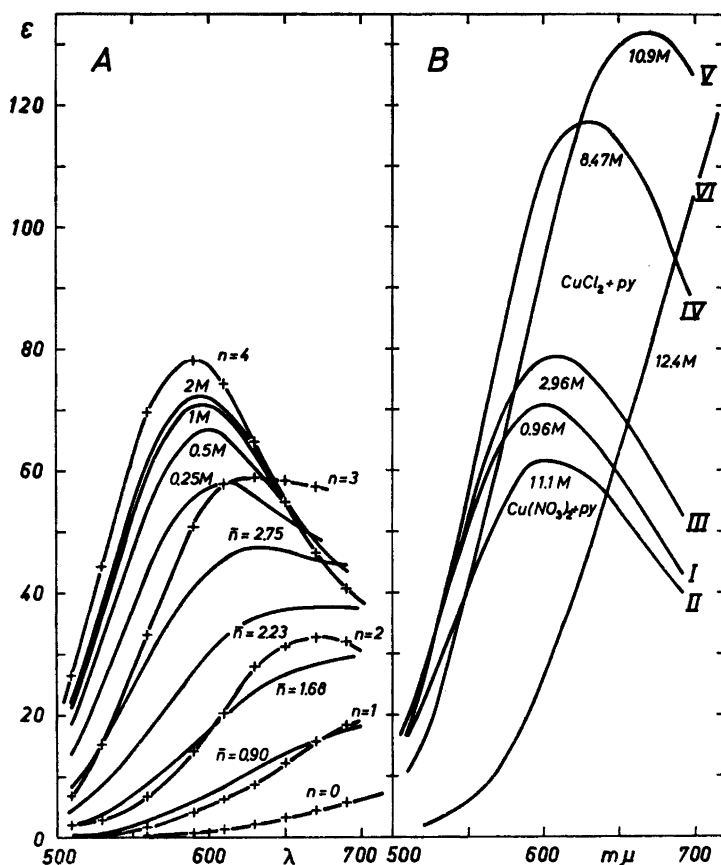


Fig. 3. Spectra of copper(II)-pyridine solutions at 23°. Molar extinction coefficients versus the wavelength in  $m\mu$ . A: Absorption curves of 0.01 M  $\text{Cu}(\text{NO}_3)_2$  in 0.5 M  $\text{pyHNO}_3$  at the total concentrations of pyridine (or values of  $\bar{n}$ ) quoted at the curves, and the calculated spectra of  $\text{Cu py}_n^{2+}$  for  $n = 1, 2, 3,$  and  $4$  (+ points). B: Absorption curves of 0.01 M copper(II) solutions in aqueous pyridine without pyridinium salt. Curves I–II with 0.01 M  $\text{Cu}(\text{NO}_3)_2$ , and III–VI with 0.01 M  $\text{CuCl}_2$ . The pyridine concentrations (quoted at the curves), and the water concentrations, respectively, were the following: No.,  $C_{\text{py}}, C_{\text{H}_2\text{O}}$ ; I, 0.96 M, 51.3 M; II, 11.1 M, 6.2 M; III, 2.96 M, 42.8 M; IV, 8.47 M, 18.2 M; V, 10.9 M, 6.3 M; VI, 12.4 M (pure pyridine).

does not hold in more concentrated pyridine where nitrate and chloride solutions behave very differently as shown in Fig. 3 B. As already mentioned, the lowering of the band of  $[\text{Cu py}_4](\text{NO}_3)_2$  in concentrated pyridine (*cf.* curve II with  $C_{\text{py}} = 11.1$  M, and  $C_{\text{H}_2\text{O}} = 6.2$  M) is probably caused by ion-pair formation between the pyridinated copper(II) ion and the nitrate ion. Similarly, in the chloride containing solutions, the strong increase of the absorption with only slight displacement of the band up to  $C_{\text{py}} \sim 8$  M (curve IV) probably is mainly a result of ion-pair or ion-triplet formation. The subsequent strong displacement of the band towards red as the solvent approaches pure pyridine is probably

caused by real chloro-complex formation with simultaneous displacement of pyridine. Evidence for the existence of a dichlorodipyridine copper(II) complex in pure pyridine (curve VI), where  $\epsilon_{\max}$  according to Williams *et al.*<sup>25</sup> is situated at 770  $m\mu$ , is based on the following facts: Copper(II) chloride in pure pyridine is undissociated according to the boiling point criterion,<sup>26,27</sup> it has practically no electric conductivity,<sup>28</sup> and yields blue beedles of the composition  $\text{CuCl}_2 \cdot 2\text{py}$ .<sup>28</sup> Finally, the displacement of the band from 590  $m\mu$  to 770  $m\mu$  would be expected from ligand field theory<sup>29</sup> for the exchange of two pyridine molecules in  $\text{Cu py}_4^{2+}$  with chloride ions.

### EXPERIMENTAL

*Vapour pressure measurements.* For the pyridine vapour pressure measurements, a very accurate gas measuring instrument, "The Boys Bell Meter", from Griffin and Tatlock, Ltd., London, was used. This instrument differs in construction from that of the usual form of wet test meter in having the measuring drum placed within a bowl covered with a glass bell so that the operation of the drum was visible to the user, and in having the axle of the drum running on bearings in the water of the meter, so that there was no 'stuffing box' friction and no need for lubrication. As the water level was above the junction between the glass bell and the bowl, leakage of gas was impossible. The instrument was equipped with a revolution counter and, correctly adjusted, the drum gave 0.700 liter per revolution.

The meter was used in a room with nearly constant temperature, and the absorption vessels were placed in a water thermostat at 25°C. The procedure was as follows: Nitrogen from a cylinder (carbon dioxide-free and saturated with water vapour at 25°) was led through a large Friedrich's absorption flask containing about 100 ml of the pyridine solution, then through two absorption vessels containing titrated amounts of 1 M acid, and finally through the meter. The transferred pyridine was almost exclusively absorbed in the first acid-containing vessel. The pyridine absorbed was determined by back-titration with 0.930 M NaOH from a microburette, and is given in Table 1 as ml of 0.930 M NaOH. The volume of gas (in liter) recorded by the meter was converted from the measured room temperature and barometric pressure to 25° and to the pressure of the gas (about 6 mm of Hg higher than the barometric pressure) as it left the pyridine solution. Denoting the corrected volume as vol, the pressure in mm of Hg is given by the expression:

$$p = \frac{\text{ml} \times 0.930}{\text{vol} \times 1000} \times 24.47 \times 760$$

where 24.47 liter is the molar gas volume at 25° and 760 mm of Hg. The pyridine concentration in the absorption flask, corresponding to the observed pressure, was taken as the average during an experiment, subtracting from the initial concentration a correction for half of the transferred pyridine, and, when two or three experiments were performed with the same solution, the appropriate corrections were introduced (see Table 1).

The method and procedure were tested by measuring the ammonia vapour pressure of a 0.500 M ammonia solution, and the  $p_{\text{NH}_3}/[\text{NH}_3]$  was determined to be 13.20 in good agreement with the findings of Scheffer and de Wijs.<sup>30</sup>

*Glass electrode measurements.* These measurements were performed as previously described<sup>31</sup> with a Radiometer potentiometer, PHM 3. The glass electrode was proved to have theoretical pH-dependence, and the whole set-up was placed in an air thermostat at 25°C.

*Spectrophotometric measurements.* The absorption spectra were measured with a König-Martens Spectrophotometer equipped with the "grosse Beleuchtungseinrichtung".<sup>4</sup> This instrument is more laborious to work with than the more modern spectrophotometers, but, in the wavelength range examined, its accuracy was not inferior to that of the Beckman DU.

*Solutions.* The various solutions were prepared in calibrated measuring flasks by weighing or pipetting from stock solutions. For the copper nitrate and chloride solutions

in concentrated pyridine all additions to the measuring flasks were made by weight, and in some cases water was removed by evaporation in a desiccator before filling up the flasks with pyridine. *Pro analysi* chemicals were used except in the case of the pyridine, which was purified and analyzed as follows: Pyridine (de Haën, doppel gereinigt) was distilled with potassium permanganate, dried with solid potassium hydroxide, and distilled through a column. The boiling range of the fraction collected was 115.4–115.5°C, and the equivalent weight was determined to be 79.1, in good agreement with the theoretical value 79.05. Stock solutions of pyridinium nitrate were prepared by neutralizing the pyridine with 5 M nitric acid. The excess of acid or base in the pyridinium nitrate stock solutions was determined by pH-measurements, and a correction was also made when necessary for the selfdissociation of the pyridinium salt by means of the formula:  $C_{py}(\text{corr.}) = C_{py}(\text{add.}) + K_a C_{pyH^+} / C_{py}$ , and correspondingly for  $C_{H^+}$ .

*Analysis.* Copper in the copper(II) nitrate stock solution was determined by electrolysis, and pyridine by acid-base titration with 1 M standard solutions to the theoretical pH.

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