cyanate ions, the complexes of copper and pyridine homologs are extracted into chloroform. It has been reported that copper complexes containing homologs of pyridine are not extracted into chloroform.[14] The colored chloroform extracts show interesting variations as far as absorption maxima are concerned. These maxima are listed in Table IV. This striking anion specificity is also exhibited by the ferrous–phenanthroline system.[24]

TABLE IV

ABSORPTION MAXIMA (mμ) FOR $CHCl_3$ EXTRACTS OF Cu(II) COMPLEXES

Ligand	Cyanate	Thiocyanate
Pyridine	680	410
2-Picoline	640	425
3-Picoline	700	410
4-Picoline	690	400
2,3-Lutidine	640	430
2,4-Lutidine	640	420
2,6-Lutidine	630	425

A study of the data shows that substitution of a methyl group in the alpha position on the pyridine nucleus causes a shift of 40 mμ toward shorter wave lengths for the complexes with cyanate ion. The same substitution causes a shift of 10–20 mμ toward longer wave lengths for complexes with thiocyanate ion. Substitution in the various other positions has little effect upon the absorption maximum of the complex. In multiple substitution, the variations are due almost entirely to the methyl group in the ortho position to the nitrogen atom. The difference in the direction of the wave length shift is quite unexpected since these ions are two of the very few capable of bringing about the extraction. This relationship would have made a close relationship in the changing of the wave length seem more probable. Apparently there is no direct correlation between the two phenomena. The marked effect of the ortho substitution suggests a steric involvement since *para* substitution should produce similar changes in electronic distribution.

Effect of Reductants.—It was observed that all of the coördination compounds of copper(II) ion reacted with reducing agents to form coördinated compounds of the copper(I) ion. Reduction was effected in basic solution with such reducing agents as hydroxylamine hydrochloride and sodium hyposulfite. Reduction occurred in solutions made basic with either ammonia or an alkali hydroxide. No reaction occurs in acidic solution. This indicates a markedly different relationship between the copper(II) and copper(I) complexes in acidic environment as compared to basic solution. This may be due in part to the effect of the close association of the hydroxyl groups.

The copper(I) complexes of ammonia and the saturated polyamines studied are colorless in alkaline solution. The copper(I) pyridine complex is yellow. The combination of the lower oxidation state of copper and unsaturated polyamine ligands results in highly colored species.[25] These are predominantly yellow or yellow-red. Reduction of the oxidation state of the central metal ion in this group of coördination compounds causes a tremendous change in the absorption spectra with large increases in the color intensity of the species involved.[23] The more highly colored complexes also are the more stable.

Acknowledgment.—The authors wish to thank the United States Atomic Energy Commission for the research grant which made this work possible.

[25] G. Tartarini, *Gazz. chim. ital.*, **63**, 597 (1933).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Cadmium and Copper Complexes of Imidazole and 1-Methylimidazole[1a,b]

BY NORMAN C. LI, JAMES M. WHITE AND EDWARD DOODY[1c]

RECEIVED JULY 9, 1954

The over-all formation constants of cadmium complexes of imidazole have been determined in water at 25° and in 18.8% ethanol (by vol.) at 0, 25 and 35°. The values of $\Delta H°$ and $\Delta S°$ for the reaction $Cd^{++} + 4Im = CdIm_4^{++}$ in 18.8% ethanol are -10.8 ± 0.6 kcal./mole and -2.2 ± 0.1 cal. deg.$^{-1}$ mole^{-1}, respectively. The solvent effect of ethanol on complex formation is negligible. It is shown that the polarographic method gives the formula of the highest order complex with certainty; this is not possible with the Bjerrum *p*H treatment for the cadmium complexes of imidazole. Double waves are obtained for the copper complexes of imidazole: for $CuIm_4^{++}$, $\log k_{f,4} = 12.6$; for $CuIm_2^{+}$, $\log k_{f,2} = 10.8$. The formation constants of 1-methylimidazole complexes of cadmium and copper are of the same order as those of the imidazole complexes. These results indicate that the site of binding on the imidazole molecule is the "pyridine" nitrogen rather than the "pyrrole" nitrogen.

Introduction

Recent work[2] has shown that in the combination of cadmium and copper ion with serum albumin the principal binding sites are the imidazole groups of the histidine residues of the protein molecule. The association of imidazole itself with the ions of cadmium and copper(II) has previously been reported by Tanford and Wagner[3] and by Edsall, *et al.*,[4] respectively. These complexes were investigated by means of the potentiometric *p*H method of Bjerrum only and, at least in the cadmium complexes, the values obtained at high *p*H are so inaccurate that it is not possible to tell what the highest order complex is. For this reason an independent method of investigating complex formation is highly desirable and it will be shown in

[1] (a) This work has been supported by a grant from the National Science Foundation, Grant No. G510; (b) taken in part from the M.S. thesis of J. M. White, Duquesne University; (c) Christian Brothers College, Memphis, Tenn.

[2] C. Tanford, THIS JOURNAL, **74**, 211 (1952).

[3] C. Tanford and M. L. Wagner, *ibid.*, **75**, 434 (1953).

[4] J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, *ibid.*, **76**, 3054 (1954).

this paper that the polarographic method gives the formula of the highest order complex with certainty and moreover gives an over-all formation constant which serves as a useful check on the individual formation constants obtained by the use of Bjerrum's method.

Interactions between metals and proteins have been used to effect separation of protein components in blood plasma, and dilute alcohol solutions[5] have been used as the media. In order to see whether the metal–imidazole complexes have similar properties in aqueous as in mixed solvents, we have investigated the cadmium imidazole complexes in varying water–ethanol solvents at 0, 25 and 35°.

Finally, to obtain information about the site at which imidazole binds with metal. we also investigated the cadmium and copper(II) complexes of 1-methylimidazole.

Experimental

Material.—A sample of 1-methylimidazole was kindly supplied by Dr. R. W. Cowgill[6] of the University of California. Imidazole (m.p. 89.5–90°, lit. 90°) obtained from Eastman Kodak Co. was used without further purification, after drying for several days over anhydrous calcium chloride. Stock solutions of the imidazoles were prepared and then standardized with standard nitric acid by conductometric and pH titration. Both methods give the same result.

All the other chemicals used were of reagent grade. Stock solutions of copper(II) nitrate were analyzed by addition of excess KI and titration of the liberated iodine; stock solutions of cadmium nitrate by conversion to $CdSO_4$.

Apparatus—Polarographic measurements were made with a Sargent Recording Polarograph, Model XXI, and manually with a Fisher Elecdropode. The half-wave potentials, after correction for the IR drop, are reproducible to ±1 mv., and are determined in the manner previously described.[7] The pH was measured with a Beckman pH meter, Laboratory Model G. Solutions were maintained at a constant temperature by means of constant temperature baths at 25 ± 0.1°, 35 ± 0.1°, and by means of an intimate mixture of ice and water at 0 ± 0.1°.

Results and Discussion

In all our work, the total ionic strength of each solution is kept constant at 0.15 to correspond to the ionic strength used in metal albumin studies.

(A) Cadmium Complexes of Imidazole.—Some 20 polarograms were taken with solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.15 M KNO_3 and varying concentrations of imidazole in water at 25.0°. The data are used to calculate the number of groups, p, coördinated to each cadmium ion and the over-all formation constant, k_f, of the complex by means of the equations[7]

$$\Delta E_{1/2}/\Delta \log C_{\mathrm{Im}} = -(RT/nF)p(2.303) \quad (1)$$

and

$$(E_{1/2})_c - (E_{1/2})_s = -(RT/nF)\ln k_f - p(RT/nF)\ln C_{\mathrm{Im}} \quad (2)$$

All potentials are referred to the saturated calomel electrode (S.C.E.) and plots of $\log i/(i_d - i)$ $vs.$ E show that in each case the electrode reaction is reversible and $n = 2$.

A plot of $E_{1/2}$ $vs.$ $\log C_{\mathrm{Im}}$ in the concentration range 1.30 to 0.02 M shows that the curve can be interpreted as a composite of three straight lines. When the concentration of imidazole is relatively large (higher than 0.08 M), the line is steepest and longest, and yields $p = 3.96$. This means that the highest order complex has the formula $CdIm_4^{++}$, even when the imidazole concentration is as high as 1.30 M ($Cd(NO_3)_2$, 5×10^{-4} M). As mentioned earlier it is not possible to determine the formula of the highest order cadmium complex of imidazole by the Bjerrum pH method. For example, at $\bar{n} = 1$, an error in pH of 0.02 changes the value of $\bar{n}$ by only 0.02, whereas at $\bar{n} = 3$, the same error in pH changes the value of $\bar{n}$ by 0.2. On the basis of what has been presented, it is clear that the polarographic method gives the formula of the highest order complex with certainty.

The next two lines in the curve are relatively short (in the concentration range 0.08 to 0.04 and 0.04 to 0.02 M, respectively), and have slopes corresponding to $p = 2.91$ and $p = 2.09$. These two values of p thus reveal the presence of the complexes $CdIm_3^{++}$ and $CdIm_2^{++}$, respectively. The over-all formation constants, $k_{f,4}$, $k_{f,3}$, $k_{f,2}$ of the complexes $CdIm_4^{++}$, $CdIm_3^{++}$ and $CdIm_2^{++}$ are calculated by means of equation 2 and the average values are listed in Table I. The over-all formation constant, $k_{f,4}$, is the equilibrium constant for the reaction

$$Cd^{++} + 4Im = CdIm_4^{++} \quad (3)$$

and is equal to $k_1k_2k_3k_4$, where $k_1 = (CdIm^{++})/(Cd^{++})(Im)$; $k_2 = (CdIm_2^{++})/(CdIm^{++})(Im)$; $k_3 = (CdIm_3^{++})/(CdIm_2^{++})(Im)$; $k_4 = (CdIm_4^{++})/(CdIm_3^{++})(Im)$. Thus $\log k_{f,4} = \log k_1k_2k_3k_4$; $\log k_{f,3} = \log k_1k_2k_3$; $\log k_{f,2} = \log k_1k_2$. The values obtained by Tanford and Wagner[3] using the Bjerrum method are included in Table I for comparison. It must be emphasized that in using the pH data, only the first three formation constants of cadmium imidazole complexes can be

Table I

Constants for the Cadmium Complexes of Imidazole

	$-(E_{1/2})_s$	$\log k_{f,4}$	$\log k_{f,3}$	$\log k_{f,2}$
Cd–Im, 25° (H_2O)	0.583	7.48	6.46	5.07
		7.58 ± 0.27[a]	6.45[a]	
Cd–Im, 25° (18.8% ethanol)	.584	7.49		
Cd–Im, 25° (31.3% ethanol)	.588	7.52		
Cd–Im, 0° (18.8% ethanol)	.617	8.15		
Cd–Im, 35° (18.8% ethanol)	.574	7.20		

[a] Calculated from log k_1's of Tanford and Wagner, ref. 3. The other constants are from this investigation; their estimated accuracy is of the order of ±0.05.

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[5] E. J. Cohn, F. R. N. Gurd, D. M. Surgenor, B. A. Barnes, R. K. Brown, G. Derouaux, J. M. Gillespie, F. W. Kahnt, W. E. Lever, C. H. Liu, D. Mittelman, R. F. Mouton, K. Schmid and E. Uroma, This Journal, **72**, 465 (1950).

[6] R. W. Cowgill and W. M. Clark, *J. Biol. Chem.*, **198**, 33 (1952).

[7] (a) N. C. Li and E. Doody, This Journal, **72**, 1891 (1950); (b) *ibid.*, **74**, 4184 (1952); (c) *ibid.*, **76**, 221 (1954).

computed with any accuracy, hence the highest over-all formation constant, $k_{f,4}$, serves as a useful check on the fourth formation constant.

Polarographic data for solutions of the same composition in 18.8% ethanol (by vol.) and in 31.3% ethanol (by vol.) at 25° are close to the corresponding data for aqueous solvent at 25°. Constants calculated from these and from similar data for solutions in 18.8% ethanol at 0 and 35° are listed in Table I. The data are obtained only for solutions containing relatively high concentrations (1.30 to 0.08 M) of imidazole and the results show that the highest order complex is again $CdIm_4^{++}$, regardless of the solvent and temperature. It is seen that log $k_{f,4}$ at 25° is about the same regardless of whether the solvent is water, 18.8% or 31.3% ethanol. In addition our value of 7.20 for log $k_{f,4}$ of Cd–Im, 35° (18.8% ethanol) differs only little from the value 7.16 in water at 35°.[3] Thus the solvent effect of ethanol on complex formation of cadmium imidazole is negligible.

From the values of log $k_{f,4}$ of cadmium imidazole in 18.8% ethanol, ΔH° for reaction 3 in 18.8% ethanol is found to be -10.8 ± 0.6 kcal./mole. The combination of this value with the standard free energy changes derived from the values of log $k_{f,4}$ lead to a corresponding standard entropy change of -2.2 ± 0.1 cal. deg.$^{-1}$ mole^{-1}. It may be interesting to note that for reaction 3 in water,[3] ΔH° and ΔS° are calculated to be -12 ± 3 kcal./mole and roughly -7 cal. deg.$^{-1}$ mole^{-1}, respectively.

(B) Copper Complexes of Imidazole.—Table II summarizes the polarographic result obtained for copper complexes of imidazole, at 25° in aqueous medium. The waves resemble somewhat those obtained for copper–ammonia complexes[8] in that at high concentrations of imidazole, each polarogram consists of two waves of approximately equal height and each wave is due to a one-electron change ($E_{3/4} - E_{1/4} = -0.050$ for each wave, as compared to the theoretical value of -0.056). The same treatment accorded to copper–ammonia complex therefore is applied here.

TABLE II

POLAROGRAPHIC RESULT FOR SOLUTIONS CONTAINING $Cu(NO_3)_2$, 5×10^{-4} M; 0.02% GELATIN; 0.15 M KNO_3 AND VARYING CONCENTRATIONS OF IMIDAZOLE

C_{Im}	$+\log C_{Im}$	$-E_{1/2}$ (first wave)	$-E_{1/2}$ (2nd wave)
1.390	0.143	0.190	0.567
1.480	.170	.194	.569
1.699	.230	.201	.577
1.835	.264	.205	.582

If we regard the reaction for the first and second waves to be

$$CuIm_p^{++} + e^- = CuIm_q^+ + (p - q)Im \quad (4)$$

and

$$CuIm_q^+ + e^- + Hg = Cu(Hg) + qIm \quad (5)$$

respectively, then for the first wave we may write

$$(E_{1/2})_{c,1} - (E_{1/2})_{s,1} = -0.0591(\log k_{f,ic} - \log k_{f,ous}) - (p - q)0.0591 \log C_{Im} \quad (6)$$

and for the second wave

$$(E_{1/2})_{c,2} - (E_{1/2})_{s,2} = -0.0591 \log k_{f,ous} - q0.0591 \log C_{Im} \quad (7)$$

In these equations $(E_{1/2})_{s,1}$ is the half-wave potential of the reaction $Cu^{++} + e^- = Cu^+$, $(E_{1/2})_{s,2}$ is that for the reaction $Cu^+ + e^- + Hg = Cu(Hg)$, $k_{f,ic}$ is the over-all formation constant of the highest order cupric imidazole complex, and $k_{f,ous}$ is the constant of the highest order cuprous imidazole complex. Since the concentration of imidazole in these experiments vary from 1.30 to 1.83 M ($Cu(NO_3)_2$, 5×10^{-4} M), it may safely be assumed that only the highest order complex is present. From our result $p - q = 2$ and $q = 2$, so that $p = 4$. This definitely shows that the highest order cupric complex is $CuIm_4^{++}$ and that the highest order cuprous complex is $CuIm_2^+$.

In equations 6 and 7 the values of $(E_{1/2})_{s,1}$ and $(E_{1/2})_{s,2}$ cannot be determined experimentally, since the polarogram of a solution containing cupric ion in non-complex-forming supporting electrolyte shows only the single wave corresponding to $Cu^{++} + 2e^- + Hg = Cu(Hg)$. Kolthoff and Lingane[8] assume that the hypothetical $(E_{1/2})_{s,1}$ of the reaction $Cu^{++} + e^- = Cu^+$ is practically equal to its standard potential, $E_s^\circ = -0.079$ v. (S.C.E.) and calculate the half-wave potential of the reaction

$$Cu(NH_3)_4^{++} + e^- = Cu(NH_3)_2^+ + 2NH_3$$

to be -0.226 v. (S.C.E.), when the concentration of NH_3 is 1 M. However, the observed half-wave potential is 0.012 v. more positive than this value. The assumption that $(E_{1/2})_{s,1} = E_s^\circ$ therefore is only approximate, and a better value would be to let $(E_{1/2})_{s,1} = E_s^\circ + 0.012 = -0.067$ v. (S.C.E.). In the same way, starting from the value $E^\circ = +0.108$ v. (N.C.E.)[8] $= +0.072$ v. (S.C.E.) for the reaction $Cu^+ + e^- + Hg = Cu(Hg)$, we have obtained $(E_{1/2})_{s,2}$ as $+0.084$ v. (S.C.E.). Using equations 6 and 7, these values of $(E_{1/2})_{s,1}$ and $(E_{1/2})_{s,2}$ and Table II, we have calculated log $k_{f,ous}$ for $CuIm_2^+$ and log $k_{f,ic}$ for $CuIm_4^{++}$ to be 10.8 and 12.6, respectively, at 25° in aqueous medium. The value of log k_f, 12.6, for $CuIm_4^{++}$ agrees well with the value 12.7, which is obtained by extrapolation to 25° from the data of Edsall, *et al.*[4] The value of log k_f for $CuIm_2^+$ has not been reported elsewhere, and it is interesting to note that it is almost the same as the value for the diamino cuprous complex ion, log $k_f = 10.87$.[8]

(C) Cadmium Complexes of 1-Methylimidazole.—Table III summarizes the polarographic result obtained for cadmium complexes of 1-methylimidazole, at 25°, in aqueous medium. A plot of $-E_{1/2}$ *vs.* $-\log C_{1-MeIm}$ yields a line of slope 0.088. Since the theoretical slope corresponding to $p = 3$ is 0.0888, the complex is $CdIm_3^{++}$. The concentration of 1-methylimidazole studied here is in the region where $p = 3$ for cadmium complexes of imidazole. In the last column of Table III the values of log $k_{f,3}$, calculated by means of equation 2, are listed. It will be noticed that the formation constant is practically the same as the corresponding over-all formation constant of cadmium imidazole, log $k_{f,3} = 6.46$, listed in Table I. The

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[8] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, New York, N. Y., 1952, p. 229.

significance of this result will be pointed out in the next section. Because of the limited supply of 1-methylimidazole, we were not able to do further experiments at higher concentrations, where a higher order complex would predominate.

Table III

Polarographic Result for Solutions Containing $Cd(NO_3)_2$, 5×10^{-4} *M;* 0.15 *M* KNO_3 and Varying Concentrations of 1-Methylimidazole

$C_{1-\text{MeIm}}$	$-\log C_{\text{MeIm}}$	$-E_{1/2}$	$\log k_{f,3}$
0.0000		0.583	
.0702	1.154	.672	6.46
.0842	1.075	.680	6.52
.1053	0.978	.688	6.49
		Av.	6.49 ± 0.03

(D) Copper(II) Complexes of 1-Methylimidazole.—In this section the Bjerrum *p*H method is used. A good summary of the method has been given by Edsall, *et al.*,[4] and need not be repeated here. Titrations of copper(II) ion with 1-methylimidazole in aqueous medium were carried out at 25.0° and the results are recorded in Table IV. The *pK'* of 1-methylimidazolium ion was taken as the *p*H of the initial solution recorded in Table IV, except that the metal ion is replaced by 0.045 *M* KOH.

Table IV

Titration of Copper(II) Nitrate–1-Methylimidazole Mixtures

Initial solution: 25.00 ml. of solution containing 0.09 *M* total 1-methylimidazolium nitrate; 0.03 *M* KNO_3; 0.01 *M* $Cu(NO_3)_2$, titrated with 0.9028 *M* KOH; *pK'* of 1-MeIm = 7.20

KOH, ml.	*p*H	− log (A) (A) ≡ (1-methylimidazole)	$\bar{n}$
0.00	3.10		
.10	3.75	4.51	0.36
.20	4.17	4.12	.72
.30	4.47	3.84	1.07
.40	4.73	3.60	1.42
.50	4.97	3.38	1.76
.60	5.19	3.18	2.11
.70	5.43	2.97	2.42
.80	5.65	2.78	2.71
.90	5.86	2.60	2.99
1.00	6.03	2.45	3.25
1.10	6.23	2.29	3.43

From the data in this table, the "formation function" of the system, that is, a plot of $\bar{n}$ against −log (A) can immediately be constructed and preliminary values of log k_i read off the graph as the values of −log (A) at $\bar{n} = (-\log (A))_{\bar{n} = i - 1/2}$. This is followed by a series of successive approximations in order to obtain the final values of log k_i. From our *p*H data, because of the inaccuracy of *p*H at high $\bar{n}$ values, it is not possible to tell what the highest order complex is. In this investigation we have assumed that the maximum coordination number of copper(II) ion is 4, and have used the method developed by Professor George Scatchard for the evaluation of log k_1 and log k_4, this procedure having been shown[4] to be considerably shorter and simpler than the Bjerrum method of successive approximations.

We have plotted log *Q*, where $Q = \bar{n}/(4 - \bar{n})\cdot(A)$, as a function of $\bar{n}$ for the interaction of 1-methylimidazole with copper(II) ion, from the data of Table IV. Because of the greater error in the extreme high and low *p*H regions, some of the points in the extreme ends of the curve have been disregarded in drawing the graph. As mentioned by Edsall, *et al.*,[4] the values of log *Q* at $\bar{n} = 0$ and $\bar{n} = 4$ are the values of log χ_1 and log χ_4 respectively, where χ_1, χ_4 are the first and fourth "intrinsic constants," from which the formation constants are derived by the equations

$$k_1 = 4\chi_1;\ k_4 = \chi_4/4$$

The extrapolations of log *Q* give 3.62 and 2.81 at $\bar{n} = 0$ and $\bar{n} = 4$, respectively, from which the following values are immediately obtained: log $k_1 = 4.22$; log $k_4 = 2.21$. The extrapolations of log *Q* are attended by some uncertainty, but the values of log *k* are probably accurate to ±0.05.

In order to obtain k_2 and k_3, we have used the following procedure. From the straight line plot, it is easily seen that at $\bar{n} = 1.5$, log $Q = 3.32$, and that at $\bar{n} = 2.5$, log $Q = 3.11$. From the definition of *Q* and these values of log *Q*, the following equations may be written

$$\text{at } \bar{n} = 1.5,\ \log Q = 3.32 = \log \frac{1.5}{4 - 1.5} + pA_{(n=1.5)}$$

$$\text{at } \bar{n} = 2.5,\ \log Q = 3.11 = \log \frac{2.5}{4 - 2.5} + pA_{(n=2.5)}$$

The values of *pA* at $\bar{n}$ = 1 5 and 2.5 are easily calculated and are taken to be the values of log k_2 and log k_3, respectively. This procedure has been applied to the calculation of log k_2 and log k_3 from data on copper imidazole,[4] and the values obtained are precisely the same as those obtained by the more laborious method of successive adjustments.

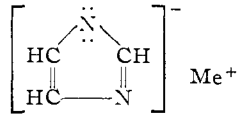
The successive values of log *k* obtained for copper(II) complexes of 1-methylimidazole are given in Table V. The values on copper imidazole complexes at 25°, obtained from the extrapolation of the data of Edsall, *et al.*,[4] at 22.4 and 4.5° are also given for comparison.

Table V

Successive Formation Constants of Imidazole and 1-Methylimidazole with Cupric Ion at 25° in Water

	1-Methylimidazole	Imidazole (extrapolated value)
log k_1	4.22	4.33
log k_2	3.54	3.54
log k_3	2.89	2.82
log k_4	2.21	2.03
log $k_{f,4}$	12.86	12.72

It is seen here that the 1-methylimidazole complexes are just as stable as the imidazole complexes. In Section C, it was shown that the cadmium complexes of imidazole and 1-methylimidazole are also equally stable. These results indicate that the site at which imidazole binds with metal is the "pyridine" nitrogen rather than the "pyrrole" nitrogen. In the case of the metal complexes of 1-methylimidazole, there would be several 1-methylimidazole molecules associated with each metal ion and, if the "pyrrole" nitrogen were the site for attachment of the metal ion, the steric effect of the methyl groups would weaken complex formation. Hoffmann[9] mentions that imidazole forms salts with metals of the general structure shown below



The complexes discussed in this paper with cadmium and copper ions, on the basis of what has been presented, cannot be expected to have this structure.

Acknowledgment.—The authors wish to express their appreciation to the National Science Foundation for support of this work. and to Dr. R. W. Cowgill for a gift of 1-methylimidazole.

Pittsburgh, Pa.

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[9] K. Hoffmann, "Imidazole," Interscience Publishers, Inc., New York, N. Y., 1953, p. 15.

[Contribution from the Department of Chemistry, The University of Wisconsin]

The Ion Exchange of Zirconium and Hafnium in Perchloric Acid with Amberlite IR-120[1]

By Edwin M. Larsen and Pei Wang

Received April 28, 1954

Batch experiments with zirconium–hafnium perchlorate solutions and Amberlite IR-120 were made over total metal ion concentrations of 1×10^{-2} to 1×10^{-5} molar, and at 2, 1 and 0.5 M perchloric acid at constant ionic strength of 2. The data show that the metal ions are hydrolyzed in the resin phase. The data can be interpreted in terms of unhydrolyzed metal species M^{+4} in the aqueous phase at 1 and 2 M hydrogen ion. The distribution data show that zirconium is favored over hafnium in the resin phase, with the ratio of the distribution coefficients, D_{Zr}/D_{Hf}, increasing in favor of zirconium at the lower aqueous hydrogen ion concentration. At high total metal ion concentration, the hafnium appears to enter into mixed zirconium–hafnium polymers at hafnium concentrations considerably below that at which the hafnium polymer formation alone would be significant.

Nearly all previous studies on the ion exchange behavior of zirconium and hafnium have been limited to investigations of the separation of these two elements.[2–7] Only a few attempts have been made to use ion-exchange resins to study the nature of zirconium species in solution. Kressman and Kitchner[8] concluded that multivalent cations in general obeyed the mass action law. However, their experiments with zirconium were very limited and apparently at very high metal ion concentrations in which case most of the metal ions in the aqueous phase must have been polymerized. Lister[9] interpreted his data as indicating the presence of polynuclear hydrolysis products in solution at low acidities, and at higher acidities, zirconium-anion complexes. He concluded that, contrary to the data of Connick, *et al.*,[10–12] there was no evidence for the existence of unhydrolyzed M^{+4} ion. We hoped that this investigation would provide an independent check on the nature of the tetravalent ions in solution and on the resin, and that any differences in behavior of zirconium and hafnium would be demonstrated.

In this research, exchange experiments were carried out using Amberlite IR-120, a sulfonic acid type cation exchanger, and zirconium–hafnium solutions 2, 1 and 0.5 M in perchloric acid. The ionic strength was maintained constant at two with sodium perchlorate. The concentration range of the total ion concentration was varied from 0.01 M to 2.5×10^{-5} M so that the exchange behavior of solutions containing both polymers and monomers[10–12] might be observed. The starting metal salt contained only a few per cent. of hafnium, so the total hafnium concentration in solution was never more than 2×10^{-4} M.

Conditions were chosen such that the hydrogen ion concentration of the solution remained essentially constant during the course of the experiment. When the aqueous solutions contained sodium ion, a mixed sodium–hydrogen resin was used which contained the equilibrium concentrations of the sodium and hydrogen ions.

The ratio of the solution volume to the resin weight was kept large, no less than 100/1, to minimize the change in solution concentrations produced by losses in solvent volume due to resin swelling.

We have chosen to express the metal concentrations in the resin phase in terms of moles of metal ion per equivalent weight of resin. For the sodium–hydrogen resin this concentration term is the same as mole fraction since these ions are univalent. The equivalent weight of the resin is that weight which contains one mole of exchangeable hydrogen or its equivalent. For the hydrogen form of Amberlite IR-120 used here, the exchange capacity was 3.73 meq./g. of air-dried resin, or 4.84 meq./g. of dry resin. The moisture content of the air-dried resin varied with composition and with the humidity, so it had to be determined with each preparation.

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[1] Based on a thesis submitted by Pei Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and carried out under Task Order 4 of Contract N7 onr-28504 between the Office of Naval Research and the University of Wisconsin.

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