Spectrophotometric Investigation of a Mixed Complex Ion Formed by Copper(II) Ion with Pyrophosphate Ion and Ethylenediamine*

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A mixed complex ion, $[Cu(P_2O_7)en]^{2-}$, has been identified in solutions containing the corresponding ratios of its constituents. The equilibrium between this mixed complex and bis-(ethylenediamine)-copper(II) ion was investigated and the logarithm of the complexity constant was found to be 17.65. An independent verification of this value was obtained by studying the degree of dismutation of the mixed complex to simple pyrophosphato and ethylenediamine complexes.

If ethylenediamine is added to a solution containing copper(II) ions and a moderate excess of pyrophosphate ions, the extinction curve shifts from that for dipyrophosphatocuprate(II) toward shorter wave lengths until, with an excess of ethylenediamine, it coincides with the extinction curve for bis-(ethylenediamine)-copper(II) ion. The extinction curves and equilibrium constants for the pyrophosphato complexes were obtained by Watters and Aaron[1] while extinction curves for the ethylenediamine complex were obtained by Bjerrum and Nielson[2] and by Jonassen and Dexter.[3] The extinctions were greater than those due to either of the above complexes in the wave length range from 740 mμ, at which the maximum for the dipyrophosphato complex occurs, and 608 mμ, which is an isosbestic for solutions containing copper(II) ions and moderate excesses of pyrophosphate ions along with one to two moles of ethylenediamine per mole of copper ion. Since this effect persisted at low pH values, it was not due to the formation of a monohydroxomonopyrophosphato complex for which Laitinen and Onstott[4] have determined the complexity constant. The proof of identity and complexity constant of the mixed complex, [Cu(P_2O_7)en]$^{2-}$, which was responsible for this effect will be presented in this paper.

The ethylenediamine complexes with copper(II) ions have been investigated by various methods. Bjerrum and Nielson[2] obtained values of 10.75 and 9.32 for the logarithms of the first and second formation constants for the complexes of copper ion with ethylenediamine at 25° and unit ionic strength using the glass electrode. They also estimated the logarithm of the formation constant for the addition of a third molecule of ethylenediamine to be −1.0 from spectrophotometric data. Schwarzenbach, Ackerman and Prue[5] verified the former results. Carlson, McReynolds and Verhoek[6] also obtained values for the first two constants using the glass electrode measurements but maintained a temperature of 30°. McCutcheon and Raymond[7] prepared four well-defined crystalline salts having the compositions CuP$_2$O$_7$·2en·2H$_2$O, Cu$_2$P$_2$O$_7$·4en·

6H$_2$O, Cu$_2$P$_2$O$_7$·3en·6H$_2$O and CuZnP$_2$O$_7$·2en·2H$_2$O, some of which may have contained the mixed complex ion. Aaron[8] found evidence for a mixed complex of copper(II) ion with ethylenediamine and pyrophosphate ion in solution by an application of Job's method of continuous variations during research on an analogous complex containing ammonia instead of ethylenediamine.[9]

The slope–intercept method of determining complexity constants spectrophotometrically which was used in the present investigation has been applied by Benesi and Hildebrand[10] to the iodine complexes with aromatic hydrocarbons. A treatment in which the higher (1:2) complex and absorption by the reactants were also considered appear in papers by McConnell and Davidson,[11] Landauer and McConnell[12] and Lawrey and McConnell.[13] In the present paper the method is extended to equilibria among three components. The symbols used by Watters and Aaron[1] and by McConnell[12,13] are retained when possible.

Experimental

Apparatus and Reagents.—The apparatus, techniques, and most of the reagents are described in the previous paper.[1] In addition, a stock solution of approximately 0.25 M ethylenediamine was prepared by transferring the proper weight of redistilled ethylenediamine (Eastman Kodak Co. 95–100%) and carbonate-free distilled water to a paraffin lined bottle. The solution was standardized with standard hydrochloric acid using brom cresol green indicator. In preparing the solutions, various volumes of this reagent were transferred to volumetric flasks by burets and other reagents were added as in the previous studies. To obtain the data used in the equilibrium calculations, all solutions were purged with nitrogen to remove CO$_2$. The buret and reagent bottle were connected by a siphon tube and both were protected from atmospheric contamination by absorption tubes filled with soda-lime. The spectrophotometric measurements were made at 10 to 20 mμ intervals with the Beckman DU spectrophotometer at 25°. The exit slit was kept as close to 0.02 mm. as the sensitivity permitted.

Experimental Procedure.—Solutions having various ratios of [Cu^{2+}]:[P$_2$O$_7^{4-}$]:[en], with the ionic strength adjusted to unity with NaNO$_3$, were prepared as before.[1] A typical series of extinction curves obtained in 1-cm. cells for solutions 5 millimolar in both CuSO$_4$ and Na$_4$P$_2$O$_7$ with varied ethylenediamine concentrations is shown in Fig. 1. The families of curves obtained with two to four pyrophosphate ion per copper ion were quite similar. With more

* From the M.S. thesis submitted by E. Dan Loughran to the Graduate School of Ohio State University.

(1) J. I. Watters and A. Aaron, This Journal, 75, 611 (1953).

(2) J. Bjerrum and E. N. Nielson, Acta Chem. Scand., 2, 297 (1948).

(3) H. B. Jonassen and T. H. Dexter, This Journal, 71, 1553 (1949).

(4) H. A. Laitinen and E. I. Onstott, ibid., 72, 4729 (1950).

(5) H. Ackerman, J. E. Prue, and G. Schwarzenbach, Nature, 163, 723 (1949).

(6) C. A. Carlson, J. P. McReynolds and F. H. Verhoek, This Journal, 67, 1334 (1945).

(7) T. P. McCutcheon and S. Raymond, ibid., 69, 276 (1947).

(8) A. Aaron, Thesis for M.S. Degree, The Ohio State University, 1952.

(9) J. I. Watters and A. Aaron, presented before the Division of Physical and Inorganic Chemistry at the convention of the American Chemical Society at Los Angeles, Calif., March 15, 1953. Portions of the present paper were also included.

(10) H. A. Benesi and J. H. Hildebrand, This Journal, 71, 2703 (1949).

(11) H. McConnell and N. Davidson, ibid., 72, 3168 (1950).

(12) J. Landauer and H. McConnell, ibid., 74, 1221 (1952).

(13) D. M. G. Lawrey and H. McConnell, ibid., 74, 6175 (1952).

than 0.05 M pyrophosphate the extinction curves corresponding to curves 1 to 6, Fig. 1 were slightly displaced toward longer wave lengths.
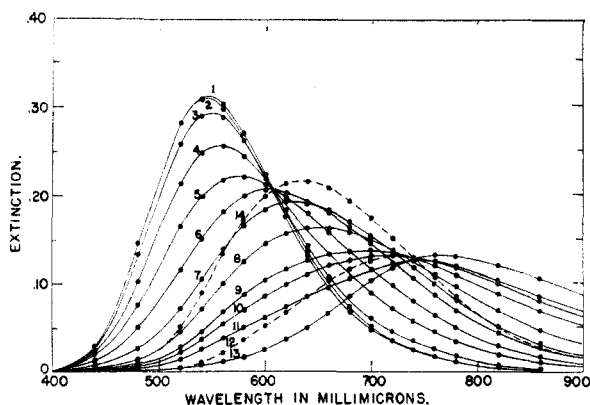

Fig. 1.—Effect of varying the ratio $[Cu^{2+}]:[P_2O_7^{4-}]:[en]$ using 0.005 M CuSO$_4$ in 1-cm. cells:

extinction, $\log_{10} I_0/I$

1,	1:1:3 or 4	2,	1:0:4	3,	1:1:2
4,	1:1:7/4	5,	1:1:3/2	6,	1:1:5/4
7,	1:1:1	8,	1:1:3/4	9,	1:1:1/2
10,	1:1:3/8	11,	1:1:1/4	12,	1:20:0
13,	1:1:0	14,	calcd., Table III, for		$[CuP_2O_7en]^{2-}$

A continuous variation experiment was performed using 0.01 M $[Cu(P_2O_7)_2]^{6-}$ and 0.01 M $[Cuen_2]^{2+}$. As shown in Fig. 2, maxima were observed at $x = 0.5$ for all wave lengths between the two isosbestic points, while minima were observed at the same value of x outside this wave length range.
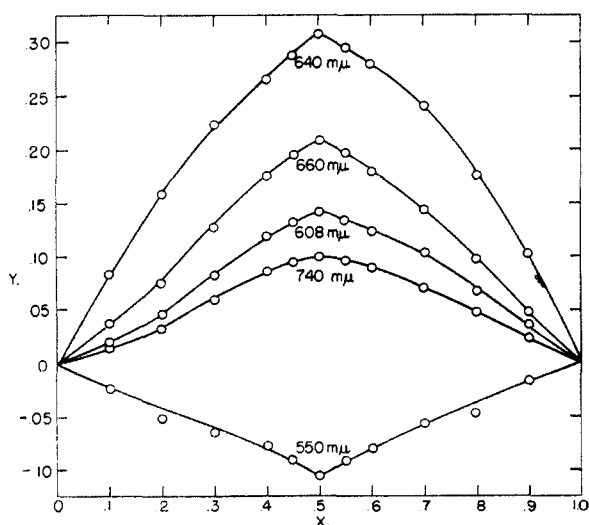

Fig. 2.—Continuous variations of $1 - x$ volumes of 0.01 M $[Cu(P_2O_7)_2]^{6-}$ with x volumes of 0.01 M $[Cu(en)_2]^2$ at different wave lengths. Y is the enhancement of the extinction due to mixed complex formation; 1-cm. cells were used.

Solutions containing mixtures of $[Cuen_2]^{2+}$ and $[Cu(P_2O_7)]^{2-}$ in equilibrium with various known ratios of free ligands were prepared as follows. A constant concentration of $C_2H_4(NH_3)_2^{2+}$ ion, 0.127 M, was obtained by the addition of the proper volumes of standardized solutions of ethylenediamine and nitric acid. The copper ion concentration was kept constant and the pH was varied by the addition of sodium pyrophosphate and perchloric acid. In Fig. 3 are shown the curves for several equilibrium mixtures of the two complexes. The experimental data are summarized in
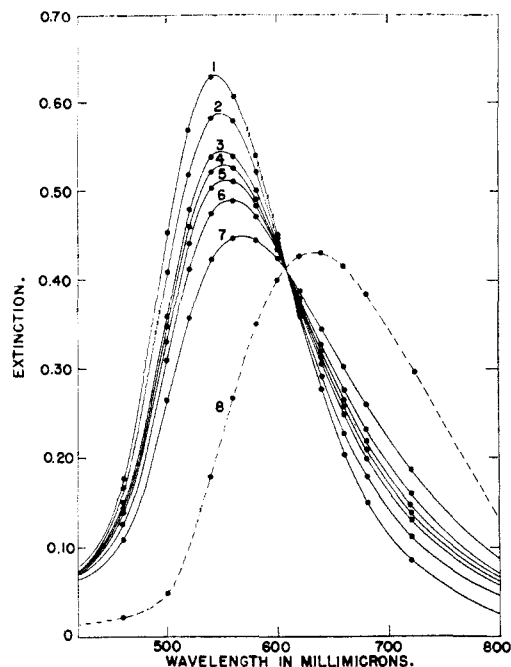

Fig. 3.—Effect of varying concentration ratio of pyrophosphate to ethylenediamine by pH adjustments; extinction $= \log_{10} I_0/I$; 10-cm. cells were used. All solutions contained 0.001 M CuSO$_4$ and 0.127 M H$_2$en^{2+}. The ionic strength was adjusted to unity with NaNO$_3$ and the following concentrations of Na$_4$P$_2$O$_7$ were added: 1, none; 2, 0.5 × 10^{-3} M; 3, 0.0015 M; 4, 0.0025 M; 5, 0.0045 M; 6, 0.1 M + H$^+$; 7, 0.1 M + H$^+$; 8, calcd., Table III, for $[CuP_2O_7en]^2$.

Table I and the effect of the ratio $[en]/[P_2O_7^{4-}]$ is shown in Fig. 4.
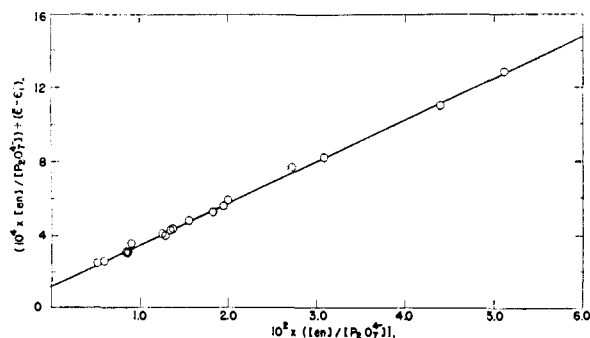

Fig. 4.—Graphic determination of equilibrium constant

Extinction data for solutions containing $[Cu^{2+}]:[P_2O_7^{4-}]:[en]$ in the ratio of 1:1:1 at various dilutions adjusted to an ionic strength of unity with NaNO$_3$ are summarized in Table II.

Discussion

All extinction curves in Fig. 1 for ratios of $[Cu^{2+}]:[P_2O_7^{4-}]:[en]$ between 1:0:4 and 1:1:1 pass through a well-defined isosbestic point at 608 mμ. A second less well-defined isosbestic point at 740 mμ was obtained for ratios in the range of 1:1:0 to 1:1:1. If only the simple complexes $[Cu\ en_2]^{2+}$ and $[Cu(P_2O_7)]^{2-}$ or $[Cu(P_2O_7)_2]^{6-}$ had been present, a minimum should have been obtained someplace between 672 mμ, where curves 2 and 13 intersect and 660 mμ where curves 2 and 12 intersect. In solutions containing at least two

TABLE I

EFFECT OF VARYING THE RATIO $[en]/[P_2O_7{}^{4-}]$ BY pH
ADJUSTMENT

All solutions: 1.0×10^{-3} M $CuSO_4$, 0.127 M $enH_2{}^{2+}$; 10-cm. cell; C_p is the total molar concentration of $Na_4P_2O_7$; E is the observed extinction $= \log_{10} I_0/I$.

$C_p \times 10^3$	pH	E at 540 mμ	$10^3 \times [en]/[P_2O_7{}^{4-}]$	$-pK_r$
0.50	5.50	0.580	5.130	2.32
1.00	5.70	.558	3.102	2.31
1.46	5.90	.538	2.735	2.22
1.99	5.90	.531	1.953	2.32
2.44	6.05	.520	1.998	2.24
2.92	6.08	.512	1.731	2.26
3.41	6.12	.511	1.562	2.30
3.98	6.10	.506	1.292	2.35
4.39	6.20	.501	1.380	2.30
4.88	6.26	.498	1.358	2.29
5.85	6.32	.491	1.260	2.29
9.90	6.42	.471	0.881	2.35
19.80	6.82	.440	.991	2.21
9.78	6.41	.472	.875	2.36
9.78	6.40	.464	.858	2.33
9.78	6.20	.420	.609	2.30
9.78	6.12	.401	.536	2.28

Av. 2.30 ± 0.06

Table II

THE DISMUTATION OF $[Cu(P_2O_7)en]^{2-}$ IN 1:1:1 SOLUTIONS
OF VARIED CONCENTRATIONS

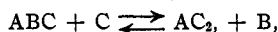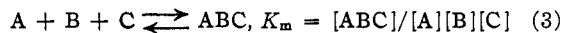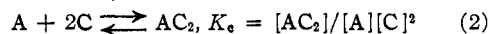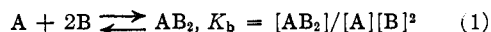| Soln. no.	C_{Cu}, M	$\bar{e}$ at 608 mμ	$\beta_2{}^a$	$\alpha_2{}^b$	$-\log K_s$
1	0.0050	37.8	0.107	0.425	1.972
2	.0050	37.1	.130	.397	1.730
3	.0075	38.0	.102	.372	1.986
4	.0100	37.4	.122	.309	1.744
5	.0150	38.6	.084	.306	2.149
6	.0200	37.8	.111	.241	1.810

Av. $-\log K_s$ 1.90

Av. β_2 0.109

^{a} β_2 is the degree of dismutation corrected for dissociation of the $[Cu(P_2O_7)_2]^{6-}$. ^{b} α_2 is the recalculated degree of dissociation of $[Cu(P_2O_7)_2]^{6-}$.

pyrophosphate ions per copper ion there should have been an isosbestic point at the latter point. The extinction in excess of that due to curve 2 from 608 to 660 mμ or in excess of that due to curve 12 from 660 to 740 mμ must be due to species other than these simple complexes. Continuous variation experiments, Fig. 2, yielded a maximum for the value $x = 0.5$, corresponding to the formula $[Cu(P_2O_7)en]^{2-}$. No other complexes were detected by this technique at any wave length.

With $[en]$ and $[P_2O_7{}^{4-}]$ of the same order of magnitude, ethylenediamine practically quantitatively displaced the pyrophosphate from the complex so it was not possible to determine the concentration of free ethylenediamine. However, by means of pH adjustments with known total concentrations of both ligands, in excess, it was possible to obtain equilibrium between $[Cuen_2]^{2+}$ and the postulated complex $[Cu(P_2O_7)en]^{2-}$. The data are summarized in Table I. The shift of the absorption curves in Fig. 3 from that of the ethylenediamine complex in curve 2 toward that of the postulated mixed complex in curve 8 corresponds with a decrease in the ratio $[en]/[P_2O_7{}^{4-}]$.

This equilibrium was verified and other information was also obtained by the previously mentioned slope–intercept method. If only solutions having extinction curves which pass through the isosbestic point at 608 mμ are considered, the treatment is simplified since the copper ion is quantitatively in the form of $[Cuen_2]^{2+}$ and some other complex postulated to be $[Cu(P_2O_7)en]^{2-}$. Consider the following equations for equilibria among three components and the corresponding complexity constants

$$A + 2B \rightleftharpoons AB_2, \quad K_b = [AB_2]/[A][B]^2 \quad (1)$$

$$A + 2C \rightleftharpoons AC_2, \quad K_c = [AC_2]/[A][C]^2 \quad (2)$$

$$A + B + C \rightleftharpoons ABC, \quad K_m = [ABC]/[A][B][C] \quad (3)$$

$$ABC + C \rightleftharpoons AC_2, + B,$$

$$K_r = [ABC][C]/[AC_2][B] = K_c/K_m \quad (4)$$

where $[A]$, $[B]$, $[C]$, $[AB_2]$, $[AC_2]$ and $[ABC]$ are the equilibrium molar concentrations of the reactants, the simple complexes and the postulated mixed complex. It is not necessary to consider intermediate complexes since an excess of ligands is present. In the present investigation A, B and C are copper ion, pyrophosphate ion and ethylenediamine.

If $[A]_0$ indicates the total concentration of A in all forms the following equation is valid for the solutions being considered

$$[A]_0 = [AC_2] + [ABC] \quad (5)$$

The extinction of these solutions is

$$\log_{10} I_0/I = E = e_m[ABC]l + e_c[AC_2]l = \bar{e}[A]_0l \quad (6)$$

where $\bar{e}$ indicates the mean molar extinction coefficient of A in all forms, while e_c and e_m indicate the molar extinction coefficients of AC_2 and ABC, respectively, at 540 mμ and l is the cell length.

Combining equations 2, 3, 4, 5 and 6 yields

$$\frac{[C]/[B]}{(\bar{e} - e_m)} = \frac{[C]/[B]}{(e_c - e_m)} + \frac{K_r}{(e_c - e_m)} \quad (7)$$

In the range of concentrations for which the postulated equilibrium is correct, a plot of $[en]/[P_2O_7{}^{4-}] \div (\bar{e} - e_m)$ along the y-axis $vs.$ $[en]/[P_2O_7{}^{4-}]$ along the x-axis will yield a straight line having a y-intercept equal to $K_r/(e_c - e_m)$ and a slope equal to $1/(e_c - e_m)$. From these values it is possible to calculate K_r and one molar extinction coefficient if the other is known.

In this particular case more accurate results were obtained by using the ratio $[C]/[B]$ in the equation even though the y-term in an equation using the reciprocal, $[B]/[C]$, would have contained the more reliable e_c for a known complex instead of e_m for the postulated complex. This was due to the fact that the relative errors in the small $(e_c - \bar{e})$ terms were larger than in the $(\bar{e} - e_m)$ terms. The mean value, 18.2 M^{-1} cm.$^{-1}$, for e_m was readily calculated from the observed value, 61.8 M^{-1} cm.$^{-1}$ for e_c (or e_{en}) and the observed extinctions of curves 3, 4 and 5, Fig. 1, using equation 6. It was later verified by equation 19.

For the postulated equilibrium, equation 4 becomes

$$[Cu(P_2O_7)en]^{2-} + en \rightleftharpoons [Cuen_2]^{2+} + P_2O_7{}^{4-} \quad (8)$$
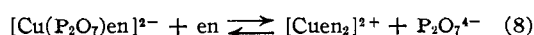
The expression for the equilibrium constant, K_r, for

this reaction, and its relation to the stability constants, K_{en} and K_m, for $[Cuen_2]^{2+}$ and $[Cu(P_2O_7)-en]^{6-}$, respectively

$$K_r = \frac{[Cuen_2{}^{2+}][P_2O_7{}^{4-}]}{[CuP_2O_7en^{2-}][en]} =$$

$$\frac{[Cuen^{2+}]}{[Cu^{2+}][en]^2} \div \frac{[Cu(P_2O_7)en^{2-}]}{[Cu^{2+}][P_2O_7{}^{4-}][en]} = \frac{K_{en}}{K_m} \quad (9)$$

Applying equation 7 to the equilibrium in equation 9 yields

$$\frac{[en]/[P_2O_7{}^{4-}]}{(\bar{e} - e_m)} = \frac{1}{(e_{en} - e_m)K_r} + \frac{1}{(e_{en} - e_m)} \frac{[\bar{e}_{en}]}{[P_2O_7{}^{4-}]} \quad (10)$$

Plot as Y   Intercept, I   Slope, S   Plot as X

where $\bar{e}$ is the mean observed molar extinction coefficient for copper ion in all forms and e_{en} and e_m are the extinction coefficients for $[Cuen_2]^{2+}$ and $[Cu(P_2O_7)en]^{2-}$, respectively.

To calculate the free pyrophosphate ion concentration, a correction was first applied for the complex bound ligand after calculating x_{en} and x_m, the fractions of the copper ion in the form of the ethylenediamine and the mixed complex, on the basis of spectrophotometric data at 540 mμ from Fig. 2 and Table I is

$$x_{en} = (\bar{e} - e_m)/(e_{en} - e_m) \quad (11)$$
$$x_m = 1 - x_{en} \quad (12)$$

Then, from the measured pH and the third and fourth successive dissociation constants for pyrophosphoric acid,[1] having the values $10^{-5.61}$ and $10^{-7.68}$, $[P_2O_7{}^{4-}]$ was calculated by the equation[1]

$$[P_2O_7{}^{4-}] = (C_p - x_mC_{cu} \times \frac{K_3K_4}{K_3K_4 + K_3a_{H^+} + a_{H^+}^2} \quad (13)$$

Similar equations were used to calculate the concentration of free ethylenediamine using experimental values, $10^{-7.27}$ and $10^{-10.03}$, as the constants for the successive dissociation of two hydrogen ions from $C_2H_4(NH_3)_2^{2+}$, 0.127 M at an ionic strength of unity. It was necessary to use experimentally determined values for these constants since Bjerrum[2] observed that the constants changed somewhat with concentration.

The excellent linearity of all points in Fig. 4 supports the postulated equilibrium. From the slope, 2.25×10^{-2} mole^{-1} cm.$^{-1}$ and the intercept, 1.20×10^{-4}, K_r was calculated to be $10^{2.27}$. The consistency of the results is further supported by the fact that 62.4 mole^{-1} cm.$^{-1}$ for e_{en} at 540 mμ calculated on the basis of the slope agrees well with the observed value of 61.8 mole^{-1} cm.$^{-1}$. Substituting the above value for K_r and Bjerrum's[2] value of $10^{20.04}$ for the stability constant of $[Cu(en)_2]^{2+}$ into equation 9 yields a value of $10^{17.77}$ for K_m.

It was also possible to calculate K_r from the individual data in Table I using the following equation based on equation 9 since both the ratios of the ligand and complexes for each solution had been calculated. These results which are in satisfactory agreement with the graphic results are included in Table I.

$$K_r = \frac{x_{en}}{x_m} \frac{[P_2O_7{}^{4-}]}{[en]} = 10^{2.30} \pm 10^{0.06} \quad (14)$$

Substituting the mean value, $10^{2.30}$, into equation 9 yields the value $10^{17.74}$ for K_m, which is nearly identical with the previous value.

The magnitude of K_m led to the most interesting prediction that the mixed complex with no excess of either ligand should undergo dismutation into the two simple complexes to the extent of about 11% if dissociation is neglected. The experimental observation of this effect led to a completely independent method of calculating the stability constant of the mixed complex. The failure of curve 7, Fig. 1, for the 1:1:1 solution to pass through the isosbestic point at 608 mμ is due to dismutation.

The following chemical equation and equilibrium expression can be written for the dismutation of the mixed complex

$$2[CuP_2O_7en]^{2-} \rightleftharpoons [Cuen_2]^{2+} + [Cu(P_2O_7)_2]^{6-} \quad (15)$$
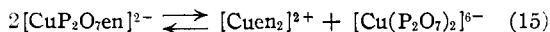
$$K_s = \frac{[Cuen_2{}^{2+}][Cu(P_2O_7)_2{}^{6-}]}{[CuP_2O_7en^{2-}]^2} = \frac{K_pK_{en}}{K^2_m} \quad (16)$$

Since this expression contains no $[P_2O_7{}^{4-}]$ or $[en]$ terms, it is only necessary to determine the concentrations of the three complex species in order to obtain an independent evaluation of K_m. The concentration of the complexes can, in general, be evaluated by the simultaneous solution of a number of equations for the extinctions of a given solution at various wave lengths. However, the procedure is greatly simplified and the errors reach a minimum if the total amounts of copper ion, pyrophosphate ion and ethylenediamine in solution are 1:1:1 corresponding to the composition of the complex, $[Cu(P_2O_7)en]^{2-}$. The calculations are further simplified if the measurements are made at the isosbestic point where the molar extinction coefficients of $[Cuen_2]^{2+}$ and $[Cu(P_2O_7)en]^{2-}$ are equal. Due to the magnitude of the association constants, the degree of dissociation of these two complexes is negligible, but the dissociation of $[Cu(P_2O_7)_2]^{6-}$ to $[Cu(P_2O_7)]^{2-}$ does produce a small effect and will be considered.

If the degree of dismutation of $[CuP_2O_7en]^{2-}$ is indicated by 2β and the degree of dissociation[1] of the resulting $[Cu(P_2O_7)_2]^{6-}$ to $[Cu(P_2O_7)]^{2-}$ is indicated by α, the equilibrium concentration of $[Cu(P_2O_7)en]^{2-}$, $[Cu(en)_2]^{2+}$ and $[Cu(P_2O_7)_2]^{6-}$ in the 1:1:1 solution are $(1 - 2\beta)C_{cu}$, βC_{cu}, and $(1 - \alpha)\beta C_{cu}$, respectively, where C_{cu} is the total copper ion concentration. Substituting these values into equation 16 yields, for (1:1:1) solutions

$$K_s = \beta^2(1 - \alpha)/(1 - 2\beta)^2 \quad (17)$$

The value of β can be calculated from spectrophotometric data for the 1:1:1 solution. The extinction for this solution, curve 7, Fig. 1, is below the isosbestic at 608 mμ due to a partial dismutation which results in the formation of pyrophosphate complexes having lower extinction coefficients. Combining equations for the conservation of copper ion with the Beer's law expression for the extinction of (1:1:1) solutions at 608 mμ yields

$$\beta = \frac{e_i - \bar{e}'_{1:1:1}}{e_i - (1 - \alpha)e'_{p2} - \alpha e'_{p1}} \quad (18)$$

where primes indicate values at 608 mμ. The molar extinction coefficient, e_i, at the isosbestic point has the value of 41.2 M^{-1} cm.$^{-1}$ while the molar extinction coefficients of the mono- and dipyrophosphato complexes, e'_{p1} and e'_{p2}, have the values 5.8 and 12.0 M^{-1} cm.$^{-1}$. The observed mean

molar extinction coefficient of copper ion in all forms in the $1:1:1$ solution at 608 mμ is indicated by $\bar{e}'_{1:1:1}$. An approximate value of β was first obtained by neglecting α in equation 17, and an approximate value of α was then calculated from the first ionization constant[1] of $[Cu(P_2O_7)_2]^{6-}$ which has the value 1.7×10^{-4}. Successive solutions of these equations yielded the values for α and β given in Table II. The corresponding value for log K_s is 1.90 ± 0.20. The mean value of K_m obtained by substituting this value, Bjerrum's value,[2] 20.04, and Watters and Aaron's corrected value,[1] 13.01, for the logarithms of the stability constants of $[Cuen_2]^{2+}$ and $[Cu(P_2O_7)_2]^{6-}$ in equation 16 is 17.48, which is in fair agreement with the values 17.77 and 17.74 obtained in the pH experiments. The mean value of log K_m is accordingly 17.66 ± 0.18.

The theoretical extinction curve 14, Fig. 1, for $[Cu(P_2O_7)en]^{2-}$ was readily calculated from similar data for a series of wave lengths using the following equation based on the conservation of copper ions and Beer's law.

$$e_m = (\bar{e}_{1:1:1} - \beta e_{en} - (1 - \alpha)\beta e_{p2} - \alpha\beta e_{p1})/(1 - 2\beta) \tag{19}$$

The data for a few points are included in Table III.

The failure of curves 7 to 13, Fig. 1, to form a well-defined isosbestic point is due to two causes, dismutation of the mixed complex and dissociation of the dipyrophosphatocuprate(II) complex. Both effects become increasingly important in the curves

TABLE III

CALCULATION OF MOLAR EXTINCTION COEFFICIENT OF 0.005 M $[Cu(P_2O_7)en]^{2-}$, ($\beta = 0.11$, $\alpha = 0.425$)

mμ	e	e_{p1}	e_{p2}	e_{en}	e_m calcd.
520	14.4	1.0	0.8	55.2	10.5
560	27.8	2.2	4.4	60.2	26.6
600	37.2	5.0	10.4	43.2	40.4
620	38.2	7.4	13.6	34.0	41.6
640	38.0	10.0	17.0	25.6	43.0
660	36.8	13.4	20.2	19.0	41.9
680	33.6	17.2	23.2	13.6	38.2
700	30.8	20.6	25.0	9.4	34.8
740	23.4	25.4	25.8	5.0	25.7
780	16.0	26.2	23.6	2.4	16.6

corresponding to solutions approaching the composition of the mixed complex and are, within experimental error, of the magnitude predicted on the basis of equation 16.

The slight shift toward longer wave lengths of curves high in pyrophosphate which is barely observed in curve 1, Fig. 1, may be due to the formation of binuclear complexes. An investigation of this effect is under way.

The authors wish to acknowledge technical assistance in the preparation of papers of this series by Miss Jean McConnell, typing, Mrs. Yvonne Holsinger, drafting, and The Ohio State Photography Department, photography.

COLUMBUS 10, OHIO

The Solubility of Ethyl Acetate in Aqueous Electrolyte Solutions[1]

BY A. P. ALTSHULLER[2] AND H. E. EVERSON

The solubility of ethyl acetate in a number of aqueous alkali halide and quaternary ammonium iodide solutions has been investigated by means of the turbidimetric method at electrolyte concentrations from 0.025 to 0.400 M and in the temperature range from 20 to 40°. The experimental activity coefficients have been compared with those calculated from various equations based on the assumption of coulombic interactions. While fairly good semiquantitative agreement is found for ethyl acetate in solutions of alkali chlorides and bromides, the experimental activity coefficients for ethyl acetate in alkali fluoride solutions are somewhat higher than those found theoretically. The theoretical activity coefficients are uniformly higher than and even differ in sign from the coefficients found experimentally for ethyl acetate in alkali and quaternary ammonium iodide solutions. The additional influence of dispersion forces is discussed qualitatively. Solubility parameters, k_s, calculated from the McDevit-Long theory are compared with the k_s found experimentally. The importance in salt effect theory of the discrete structure of the solvent is discussed.

Although a number of studies have been made of the solubility of ethyl acetate in aqueous electrolyte solutions by Euler,[3] Lunden,[4] Linde,[5] Glasstone, et al.,[6a-c] and Schlesinger and Kubasowa[7] these investigations, excepting those of Glasstone and his co-workers, have been rather limited in their

scope. The work of Glasstone, et al.,[6a-c] was rather detailed, but many of the electrolyte concentrations employed were much too high to permit comparison with theory. A more serious weakness in this work lies in the poor agreement between Glasstone's solubility results for ethyl acetate in water[6a] and those of other investigators.[8] These facts made further investigation by another experimental method seem desirable, especially since the work of Glasstone, et al.,[6a-c] has been employed in the past to test various theories of the salt effect.[9-11]

(1) Based on a part of a dissertation submitted by A. P. Altshuller to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree doctor of philosophy, July, 1951.

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