

TABLE II
TRANSFERENCE NUMBER OF K^+ IN POTASSIUM IODIDE SOLUTIONS BY VARIOUS METHODS

KI concn.	Concentration of I_2	Temp., °C.	t_+	Method and author
0.975 <i>m</i>	0.00531 <i>m</i>	20	0.4900	Present investigation
0.712 <i>m</i>	0.00385 <i>m</i>	20	.4893	Present investigation
1.00 <i>m</i>	0.01 <i>m</i>	20	.486	Centrifugal field, Tolman ⁵
0.500 <i>m</i>	0	25	.4878	Concentration cells, Gelbach ¹⁰
0.01 <i>N</i>	0	25	.4884	Moving boundary, Longworth ¹¹
0.02 <i>N</i>	0	25	.4883	Moving boundary, Longworth ¹¹
0.05 <i>N</i>	0	25	.4882	Moving boundary, Longworth ¹¹
0.1 <i>N</i>	0	25	.4883	Moving boundary, Longworth ¹¹
0.2 <i>N</i>	0	25	.4887	Moving boundary, Longworth ¹¹

is negligible, from a graph of V_{KI} in solutions of pure potassium iodide against the square root of the molality; this graph in turn was plotted from values calculated by us, using the Lewis and Randall method of intercepts, from the density of potassium iodide solutions at 20° given in the "International Critical Tables"; the values of V_{KI} are probably correct to within $0.1 \text{ cm.}^3 \times \text{mole}^{-1}$. The value of V_{I_2} is that determined by Tolman⁵ for iodine in small concentration in the presence of a large excess of iodide, at 20°, and is also probably correct to within $0.1 \text{ cm.}^3 \times \text{mole}^{-1}$. The result of the calculation is cell I, $t_+ = 0.4900$; cell II, $t_+ = 0.4893$. In Table II these values are compared with values obtained by other methods.

The most accurate of these determinations are those of Longworth; they are here cited *in extenso* because they show that at a concentration of 0.2 normal, where they break off, t_+ is slowly

(10) R. W. Gelbach, *THIS JOURNAL*, **55**, 4858 (1933).

(11) L. G. Longworth, *ibid.*, **57**, 1185 (1935).

increasing with increasing concentration; this tends to diminish the gap between our results and those obtained by other methods. In any case the difference between the present results and the best modern ones would seem not to exceed 0.5%. The conclusion seems justified that the method here described might be useful for the determination of transference numbers in certain cases.

Summary

Precise measurements are described of the e. m. f. of gravity cells using the earth's field, with the electrode Pt, KI (excess) + I_2 . The transference numbers of K^+ calculated from the measured values of the e. m. f. agree with the best modern values to within 0.5%. The potentiometer used in the measurement is described in detail; it has a range of 1540 microvolts in steps of 0.01 microvolt or of 160 microvolts in steps of 0.001 microvolt.

STANFORD UNIV., CALIF. RECEIVED NOVEMBER 19, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Copper(II) and Nickel(II) Complex Ions of Diethylenetriamine

BY HELMUT M. HAENDLER

In a recent publication, Vosburgh and Cooper¹ have extended the method of continuous variations originated by Job² to include reactions in which more than one complex ion is formed from a pair of components. Measurement of absorption at pre-selected wave lengths offers means of identifying the ions present, when both components are in solutions of equimolecular concentration.

Preliminary work on the preparation of metal complexes of diethylenetriamine, $H_2N(CH_2)_2NH_2$

$(CH_2)_2NH_2$, (abbreviated dn) suggested the advisability of determining the probable composition of the ions formed in water solution by this amine and various metal ions. It was found that copper(II) and nickel(II) were the most satisfactory; other ions generally were precipitated as hydroxide.

Determination of composition was made exactly as described by Vosburgh and Cooper.¹ Maxima of curves obtained by plotting the amount of diethylenetriamine solution (x) against the difference (Y) between observed extinction and that calculated for no reaction give directly the com-

(1) Vosburgh and Cooper, *THIS JOURNAL*, **63**, 437 (1941).

(2) Job, *Ann. chim.*, [10] **9**, 113 (1928).

position of the ions present. It was found that both copper(II) and nickel(II) formed complex ions with one and two molecules of amine per atom of metal; *i. e.*, $[\text{Me dn}]^{++}$ and $[\text{Me dn}_2]^{++}$.

It has been reported^{1,2} that copper(II) and ammonia form complex ions in which the ammonia molecules occupy two and four coordination positions. Bjerrum³ finds evidence for all possible ions from $[\text{Cu}(\text{NH}_3)]^{++}$ to $[\text{Cu}(\text{NH}_3)_4]^{++}$, with a slight, but definite, tendency for the copper(II) ion to take up a fifth molecule of ammonia. On this basis, the $\text{Cu}^{++}-\text{NH}_3$ system has been considered as having a characteristic coordination number (N) of four for the copper. The system with diethylenetriamine appears to be similar. Bjerrum also finds evidence for all the possible nickel(II) ions with ammonia, from $[\text{Ni}(\text{NH}_3)]^{++}$ to $[\text{Ni}(\text{NH}_3)_6]^{++}$, and for the ethylenediamine (en) complex ions from $[\text{Ni en}]^{++}$ to $[\text{Ni en}_3]^{++}$, indicating a characteristic coordination number of six. It thus seems reasonable to conclude that in the case of the nickel complex ions, each diethylenetriamine occupies three coordination positions and that only complexes with one and two molecules of amine per metal ion are possible. The situation with the copper(II) ions is less clear. The tendency of the metal ion, however slight, to form complexes with more than four ammonia molecules suggests that the structure may be similar to that proposed for the nickel complex. It does seem improbable that only the primary amino groups could be involved, since this would necessitate assumption of an eight-membered ring. Research in progress may clarify the situation.

Experimental

All absorption spectra were measured with the Coleman D. M. Spectrophotometer and the extinctions calculated from the transmittance values obtained. Cell depth was 1.63 cm.

The diethylenetriamine was purified by fractionation, a solution prepared and standardized against hydrochloric acid, using methyl orange as the indicator, and then diluted to 0.100 M .

Copper(II) Complex Ions.—A 0.100 M copper(II) ion solution was prepared by dissolving the theoretical quantity of copper(II) acetate monohydrate to a measured volume of solution. Two or 3 drops of 6 N acetic acid were added to prevent hydrolysis. The absorption spectra were measured for solutions 0.008 M in copper acetate, and, in addition, 0.008, 0.0107, 0.016, and 0.024 M in diethylenetriamine, the latter corresponding to ratios of 1:1, 3:4, 1:2, and 1:3. The absorption spectra are shown

in Fig. 1. The 1:3 curve was almost the same as the 1:2 curve, indicating absence of ions with more than two diethylenetriamine molecules per atom of copper and indicating rather high stability for the ions actually formed.

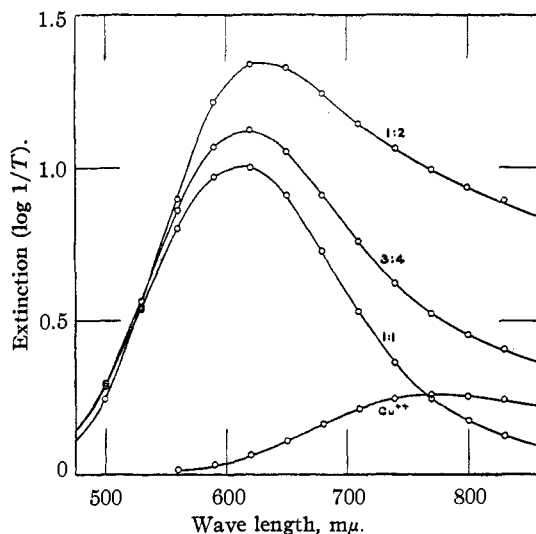


Fig. 1.—Absorption spectra of solutions containing copper acetate and diethylenetriamine in the molecular ratios 1:0, 1:1, 3:4, and 1:2.

Further measurements were then made at 490, 760, and 830 $m\mu$, selected in accordance with Vosburgh and Cooper's derivation, using variable amounts of 0.04 M solutions. The volume of diethylenetriamine solution (x) plotted against difference (Y) shows a maximum in the curve at $x = 0.5$ at 490 $m\mu$, and $x = 0.65$ at 760 and 830 $m\mu$. This indicates the ions $[\text{Cu dn}]^{++}$ and $[\text{Cu dn}_2]^{++}$. The theo-

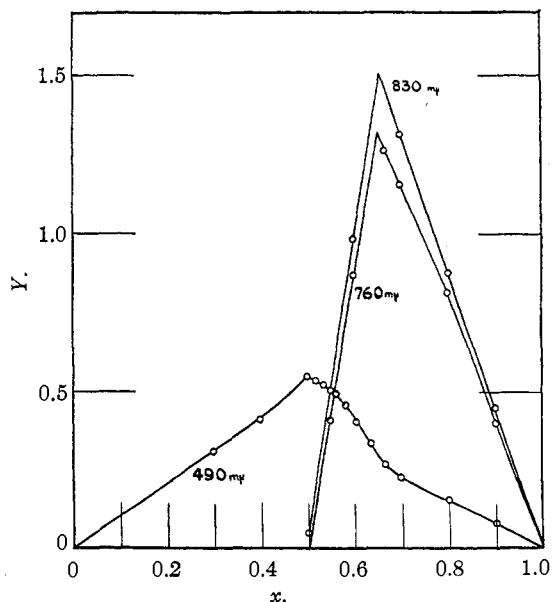


Fig. 2.— Y curves for mixtures of $(1-x)$ liters of 0.04 M Cu^{++} and x liters of 0.04 M diethylenetriamine solutions at 490, 760, and 830 $m\mu$.

(3) Bjerrum, *Chem. Abstracts*, **35**, 6527 (1941).

retical extinction for $[\text{Cu dn}^{++}]$ was calculated from the difference between the observed extinction at some low value of x (such as 0.1) and the extinction of copper(II) ion at the same point. Measurement showed that the extinction of diethylenetriamine solutions could be neglected. The Y curves are shown in Fig. 2.

Job and Brigando⁴ reported preliminary results suggesting existence of the 3:4 ion, but no evidence supporting this has been found.

Nickel(II) Complex Ions.—Fourteen grams of nickel (II) sulfate hexahydrate was dissolved in 475 ml. of water, treated for removal of cobalt,⁵ analyzed for nickel with anthranilic acid,⁶ and diluted to 0.1 M . The absorption was measured for solutions 0.025 M in nickel sulfate, and, in addition, 0.025, 0.050, and 0.075 M in diethylenetriamine. A very small amount of 6 N sulfuric acid was added when necessary to prevent precipitation of hydroxide. The spectra are shown in Fig. 3. Again the 1:3 curve indicated that 1:2 is the limiting ratio.

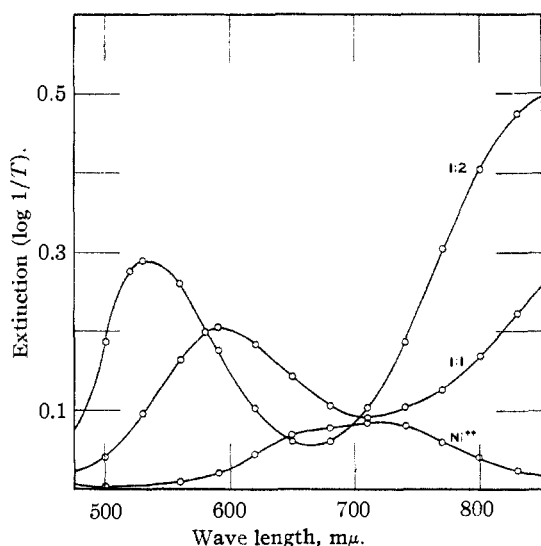


Fig. 3.—Absorption spectra of solutions containing nickel sulfate and diethylenetriamine in the molecular ratios 1:0, 1:1, and 1:2.

Measurements were then made at 540, 580, and 820 $m\mu$, using 0.1 M solutions, and maxima were obtained at

- (4) Job and Brigando, *Compt. rend.*, **210**, 438 (1940).
 (5) Deakin, Scott and Steele, *Z. physik. Chem.*, **69**, 126 (1909).
 (6) Funk and Ditt, *Z. anal. Chem.*, **93**, 241 (1933).

$x = 0.5$ at 580 $m\mu$, $x = 0.66$ at 540 $m\mu$, and $x = 0.67$ at 820 $m\mu$, corresponding to $[\text{Ni dn}]^{++}$ and $[\text{Ni dn}_2]^{++}$. The curves are shown in Fig. 4.

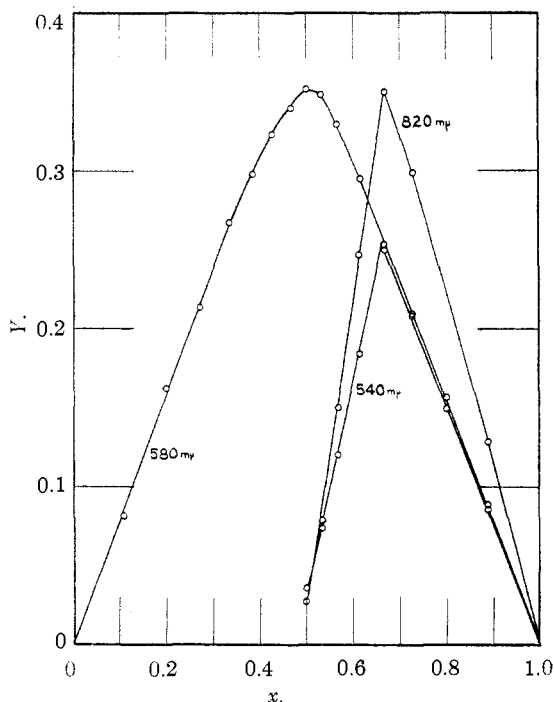


Fig. 4.— Y curves for mixtures of $(1-x)$ liters of 0.1 M Ni^{++} and x liters of 0.1 M diethylenetriamine solutions at 540, 580, and 820 $m\mu$.

Summary

The method of continuous variations of Vosburgh and Cooper has been used to study the complex ions of copper(II) and nickel(II) with diethylenetriamine.

Evidence has been found indicating the existence of the ions $[\text{Cu dn}]^{++}$, $[\text{Cu dn}_2]^{++}$, $[\text{Ni dn}]^{++}$, and $[\text{Ni dn}_2]^{++}$ in water solution.

It appears probable that each diethylenetriamine molecule occupies three coordination positions in these ions.

SEATTLE, WASHINGTON

RECEIVED NOVEMBER 7, 1941