around gadolinium which is not paralleled by the curve of the radii. It is true that there is an irregularity in the radii curve at erbium if the published radii are plotted against atomic number, but this may be accidental and due to errors connected with measuring the radii to ±0.01 Å. unit.

The break in the curve of the log K_{MY} observed at the point of gadolinium (substantiated by the change in slope when the "*a*" values as shown in Table I are plotted against *p*H for the individual rare earths) might be explained as follows: the carboxylate groups of the anion Y^{-4} are bulky groups and will have difficulty in finding enough room around the rare earth cation during coördination. This difficulty will increase as we go up the series because of the decrease in size of the cation. There should be a critical point after which no longer all four, but only three, of the $-COO^-$ groups can be coördinated. This must cause a break in the curve log K_{MY} *versus* atomic number. With gadolinium and the lighter members below it, the anion Y^{-4} will probably function as a hexadentate group. Going up the series from lanthanum to lutecium, the growing steric hindrance mentioned will prevent a large increase in stability, until at the point of gadolinium the complexing agent can no longer function as a hexadentate group, but only as a pentadentate group. From this point upward, the stability increases again steadily as the ionic radius becomes smaller. A new steric hindrance does not seem to take place in the range gadolinium to lutecium.

AMES, IOWA

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. II. Copper(II) Complexes with 2-Carboxyphenyl-azo-β-naphthol and 2-Carboxyphenyl-azo-β-naphthylamine

BY HANS B. JONASSEN AND JOHN S. WILSON

RECEIVED MARCH 2, 1953

The azo dyes, 2-carboxyphenyl-azo-β-naphthol and 2-carboxyphenylazo-β-naphthylamine were treated with copper(II) ion. A one to one reaction ratio was established in both cases by the method of continuous variation and by conductometric titrations. Evidence was advanced supporting the postulated structure involving the displacement of a hydrogen ion from each ortho substituted group of the dyes. On the basis of spectrophotometric measurements a monohydroxy addition complex was postulated for the copper(II)-2-carboxyphenyl-azo-β-naphthol compound and a dihydroxy complex for the copper(II)-2-carboxyphenyl-azo-β-naphthylamine.

Introduction

Many metal lakes of the azo dyes have been prepared but few studies of these lakes are reported in the literature. The lakes are formed between coördinating metal ions and azo dyes substituted in the ortho position by groups such as the carboxy, hydroxy, or amino. The metal ion is postulated to react with the dye by replacing hydrogen ions in the substituent groups and coördinating to the azo group.[1]

It is well known that the introduction of certain metal ions to an azo dye, used for dyeing cotton, produces better colors and greater resistance to fading. This increased stability may be explained on the basis of coördination. The dye may not occupy all the positions in the coördination sphere of the metal ion. These unoccupied positions may be occupied by hydroxy groups of the cellulose fiber thus creating a chemical bond between the fiber and the mordant dye.

This study has attempted to show by spectrophotometric and conductometric methods that the unoccupied positions in the copper(II) coördination sphere of copper(II) azo dye complexes may be occupied by free hydroxy groups. A previous study[2] of the copper(II) complex of *o,o'*-dihydroxyazobenzene has been reported, verifying the postu-

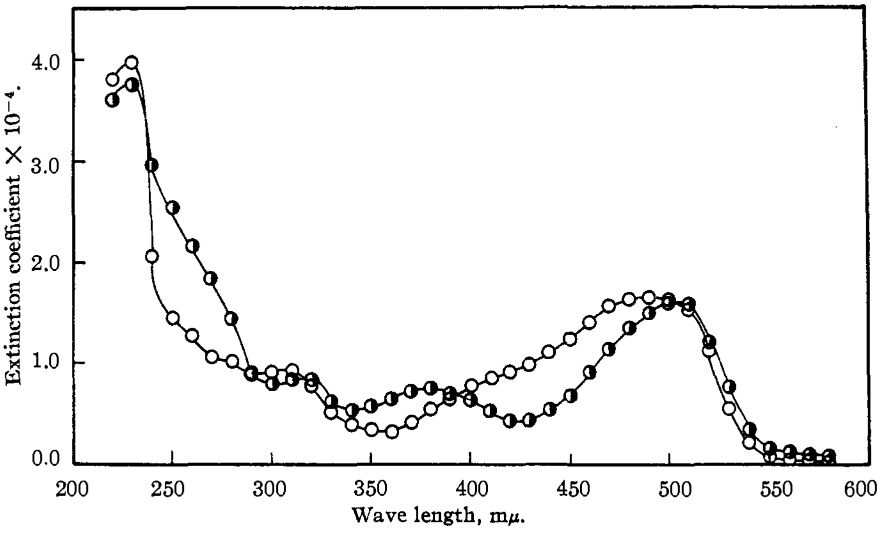

Fig. 1.—Absorption spectra of 2-carboxyphenyl-azo-β-naphthol, ○ and Cu(II)-2-carboxyphenyl-azo-β-naphthol, ◑. Temperature = 30°; 1-cm. matched corex cells; 95% ethanol solutions.

---

[1] M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

[2] H. B. Jonassen, Mae M. Cook and J. S. Wilson, THIS JOURNAL, **73**, 4683 (1951).

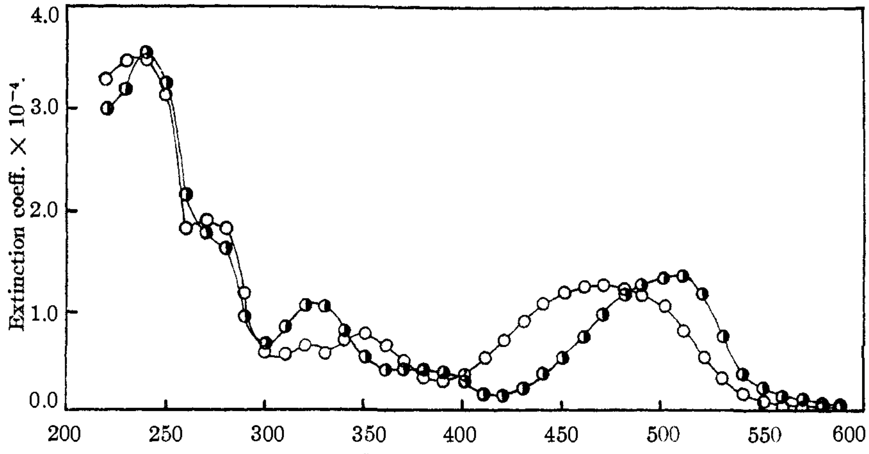

Fig. 2.—Absorption spectra of 2-carboxyphenyl-azo-β-naphthylamine, ○ and Cu(II)-2-carboxyphenyl-azo-β-naphthylamine, ◑. Temperature = 30°; 1-cm. matched corex cells; 95% ethanol solutions.

lated structure and indicating the dissolution of the complex in strongly alkaline solutions. The study is now extended to the copper(II) complexes of 2-carboxyphenyl-azo-β-naphthol and 2-carboxyphenyl-azo-β-naphthylamine.

Beech and Drew[3] reported the preparation of two lakes of the copper(II) ion and the naphthol dye. When copper(II) chloride was used as the source of the copper(II) ion, a one to one lake resulted. However, the substitution of copper(II) acetate for the copper(II) chloride gave a lake containing two copper(II) ions for each molecule of dye. The same authors reported the preparation of a one to one complex between copper(II) ion and the naphthylamine dye. In all cases these results were based upon analytical data only.

I. Absorption Studies

A. **Experimental.**—Absorptions were determined between the wave lengths of 220 and 800 mμ with a Beckman spectrophotometer, model DU, using 1-cm. matched corex cells and standard solutions of 1×10^{-4} *M* in 95% alcohol. The two dyes were prepared according to the literature.[4,5] The naphthol dye was recrystallized from 95% alcohol, m.p. 272–273°; the naphthylamine dye from benzene, m.p. 182–183°. J. T. Baker C.P. Analyzed $CuCl_2 \cdot 2H_2O$ and $Cu(C_2H_3O_2)_2 \cdot H_2O$ were dried for 24 hours over partially dehydrated $CuSO_4 \cdot 5H_2O$.

The reaction ratio of the dyes with copper(II) ion was studied using the method of continuous variation as modified by Vosburgh and Cooper.[6] Alcoholic solutions in varying proportions of 1×10^{-4} *M* dye and 1×10^{-4} *M* $CuCl_2 \cdot 2H_2O$ were prepared such that the total solute concentration was the same in all cases. The optical densities (O.D. = log (1/transmittance)) of the resulting solutions were measured and compared with the calculated optical densities. The solutions containing the naphthylamine dye were measured at 320 and 520 mμ, those of the naphthol dye at 360 and 440 mμ.

B. **Discussion of Results.**—Figure 1 shows the absorptions of the naphthol dye and a one to one mixture of the dye and $CuCl_2 \cdot 2H_2O$. The absorption of the latter (1×10^{-4} *M*), alone, was below 0.02 at all wave lengths measured. Similar measurements for the naphthylamine dye are shown in Fig. 2.

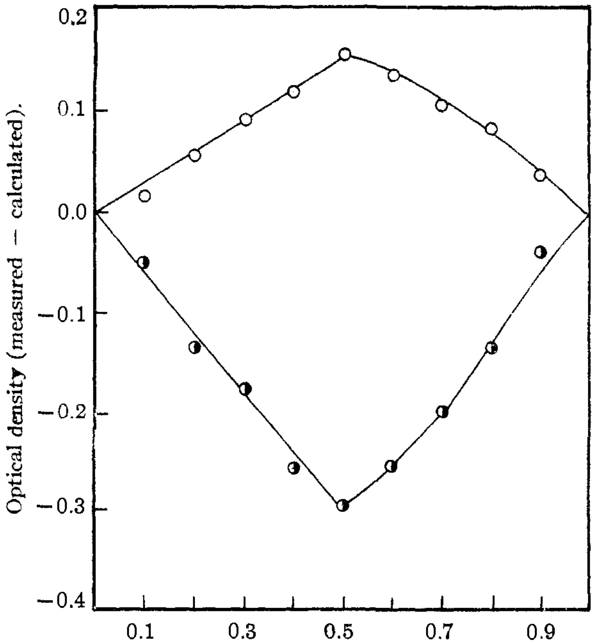

Fig. 3.—Method of continuous variation: naphthol dye and $CuCl_2 \cdot 2H_2O$. Optical density = log (1/transmittance); 1-cm. matched corex cells; 95% ethanol solution; temperature = 30°; ○, 360 mμ; ◑, 440 mμ.

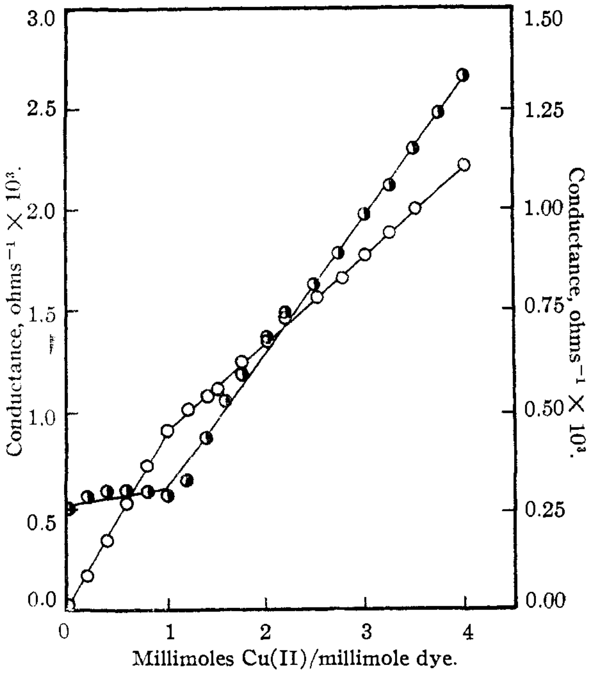

Fig. 4.—Conductometric titration: 0.02 millimole of alcoholic naphthol dye with 0.01 *M* $CuCl_2 \cdot 2H_2O$ and 0.01 *M* $Cu(C_2H_3O_2)_2 \cdot H_2O$. Scale on right refers to $Cu(C_2H_3O_2)_2 \cdot H_2O$. Temperature = 28°; ○, chloride; ◑, acetate.

---

(3) W. F. Beech and H. D. K. Drew, *J. Chem. Soc.*, 608 (1940).

(4) R. Anschütz and O. Schmidt, *Ber.*, **35**, 3463 (1902).

(5) O. Fischer, *J. prakt. Chem.*, **107**, 16 (1924).

(6) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

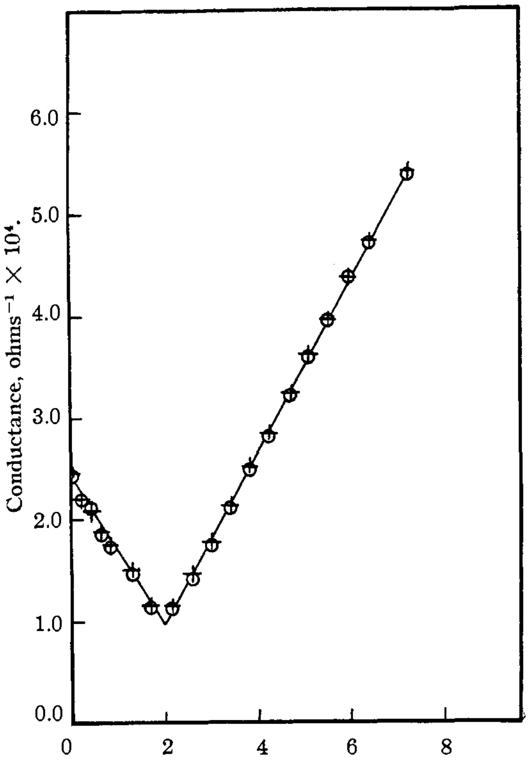

Fig. 5.—Conductometric titration: 0.05 millimole of alcoholic Cu(II)-naphthol complex and 0.05 millimole of alcoholic Cu(II)-naphthylamine complex with alcoholic 0.0210 *M* KOH. Temperature = 28°; +, naphthol complex; O, naphthylamine complex.

The difference between the calculated optical density and the observed optical density was plotted against mole fraction of dye in Fig. 3 for the naphthol dye.

Similar results were obtained for the naphthylamine dye. Since a maximum in the observed and calculated values occurs in each case at a mole ratio of one dye molecule to one copper(II) ion, one to one complex compounds must be formed. This conclusion of a one to one complex is in agreement with analytical results.[1,3]

The naphthol dye was further investigated using the same method but substituting $Cu(C_2H_3O_2)_2 \cdot H_2O$ for the $CuCl_2 \cdot 2H_2O$. A maximum difference in calculated and observed optical density values was obtained at a mole ratio of one dye molecule to one copper(II) ion. Again the formation of a one to one compound is indicated. The compound postulated by Beech and Drew[3] containing two copper(II) ions per molecule of dye could not be substantiated.

II. Conductometric Studies

A. **Experimental.**—The conductances of the solution were measured by Kohlrausch's method, using a cell with vertical platinized electrodes.

Due to the low solubility of the naphthol dye, its alcoholic solutions were titrated conductometrically with aqueous solutions of $CuCl_2 \cdot 2H_2O$ and $Cu(C_2H_3O_2)_2 \cdot H_2O$ at 28°. Figure 4 shows the plot of the conductance values obtained.

For the naphthylamine dye an aqueous solution of $CuCl_2 \cdot 2H_2O$ was titrated at 28° with a 0.01 *M* solution of the dye, and similar results were obtained. The complex precipitated immediately in the aqueous solution as a reddish-brown flocculent solid.

B. **Discussion of Results.**—Breaks in the conductance curves at the ratio of one copper(II) ion per molecule of dye in all titrations indicate the formation of one to one complexes between the copper(II) ion and each of the dyes. The shape of the conductance curves indicates the displacement of hydrogen ions of the substituent groups of the dyes by the copper(II) ion.

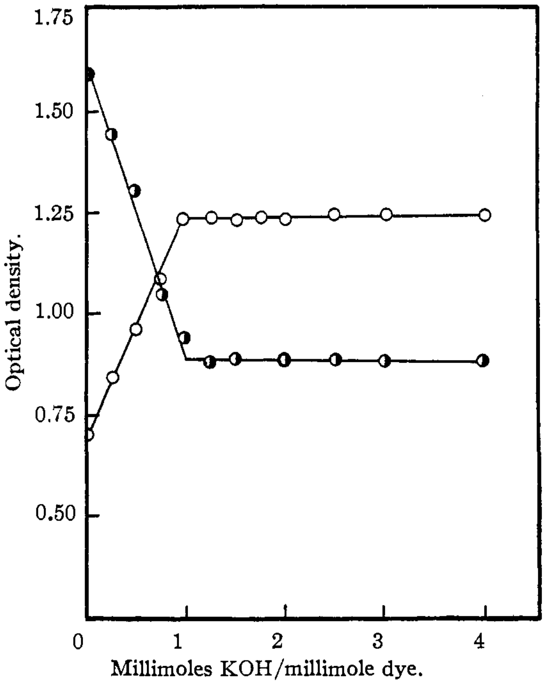

Fig. 6.—Effect of KOH on optical density of alcoholic naphthol and naphthylamine dyes: optical density is log (1/transmittance); 1-cm. matched corex cells; 95% ethanol solutions; temperature = 30°; O, naphthyl dye, 520 mμ; ◑, naphthylamine dye, 510 mμ.

Conductometric titrations of alcoholic solutions of each of the complexes prepared by mixing $CuCl_2 \cdot 2H_2O$ and dye solutions in equivalent proportions at 28° with alcoholic potassium hydroxide are plotted in Fig. 5. The two curves

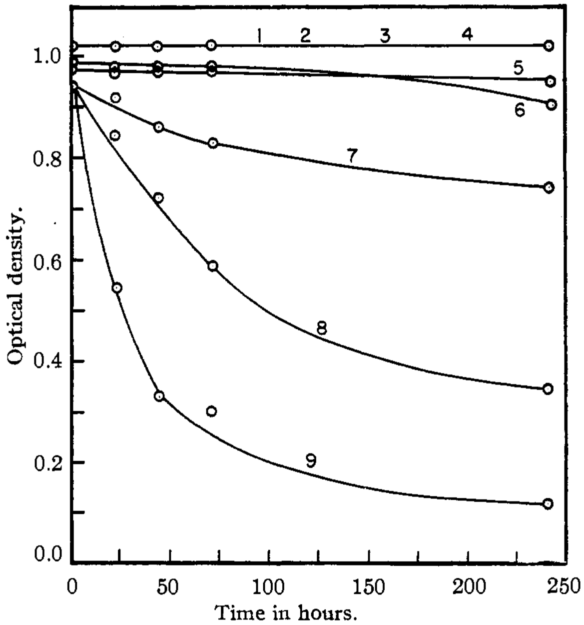

Fig. 7.—Effect of KOH on optical density of alcoholic Cu(II)-naphthol dye complex; wave length 500 mμ; temperature 30°; optical density = log (1/transmittance); 1-cm. matched corex cells; 95% ethanol solutions.

Curve	KOH:Cu-dye	Curve	KOH:Cu-dye
1	0:1	5	4:1
2	1:1	6	5:1
3	2:1	7	6:1
4	3:1	8	7:1
		9	9:1

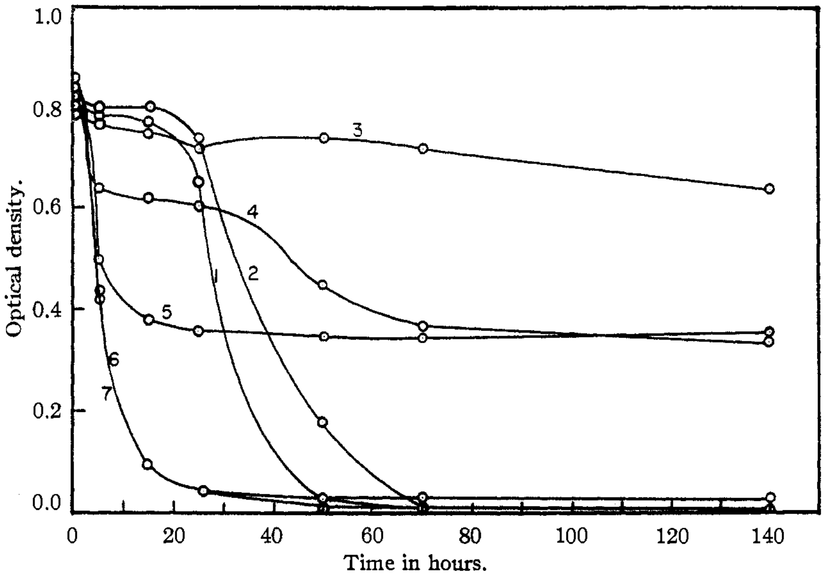

Fig. 8.—Effect of KOH on optical density of alcoholic Cu(II)-naphthylamine dye complex; wave length 510 mμ; temperature 30°; optical density = log (1/transmittance); 1-cm. matched corex cells; 95% ethanol solutions.

Curve	1	2	3	4	5	6	7
KOH:Complex Ratio	0:1	1:1	2:1	3:1	4:1	5:1	6:1

are identical with a break in each curve at the ratio of two millimoles of potassium hydroxide per millimole of complex. This break indicates the presence in the solution of two millimoles of hydrogen ion per millimole of complex. This is in agreement with the postulated structures for the complexes in which the copper(II) ion displaces a hydrogen ion from both substituent groups ortho to the azo linkage.

III. Spectrophotometric Titrations

A. **Experimental.**—Alcoholic 1×10^{-4} *M* solutions of each of the two dyes were prepared with varying amounts of potassium hydroxide. The optical densities of the naphthol dye solutions were measured at 520 mμ and those of the napthylamine dye at 510 mμ.

The optical density values plotted in Fig. 6 show a break in each case at one millimole of potassium hydroxide per millimole of dye. The carboxy group of each dye would be expected to react with potassium hydroxide. Only one hydrogen ion is replaceable in the naphthol and naphthylamine by potassium hydroxide, but the copper(II) ion apparently displaces two hydrogen ions, possibly through a mechanism such as that proposed by Burawoy.[7]

Strongly alkaline solutions of the copper(II) complexes of the dyes had been observed to lose their color on standing. A series of 5×10^{-5} *M* solutions of each complex was prepared by mixing equivalent amounts of $CuCl_2 \cdot 2H_2O$ and dye in 95% alcohol and then bubbling with nitrogen for two hours to remove oxygen. Each solution of a series was made to different alkalinity with potassium hydroxide. The optical densities of the solutions were measured at 500 mμ for the naphthol complex and at 510 mμ for the naphthylamine complex. The solutions were then placed in the dark with the temperature maintained at 30°. From time to time the optical densities were redetermined.

B. **Discussion.** 1. **Naphthol Complex.**—The changes in optical density values of the naphthol complex solutions with time are shown in Fig. 7. No change was observed until after three millimoles of potassium hydroxide per millimole of complex had been added. Past three equivalent amounts the degree of color change was proportional to the amount of potassium hydroxide added.

The first two millimoles of hydroxide ion per millimole of naphthol complex are taken up by free hydrogen ions in the solution. Since the third hydroxide ion produced no fading, it is postulated to have reacted with the complex occupying the fourth position in the coördination sphere of the copper(II) ion. This forms then a copper(II)-dye-hydroxy complex.

2. **Naphthylamine Complex.**—The data for the naphthylamine complex are plotted in Fig. 8. As curves one and two of Fig. 8 indicate, the complex decomposed in the absence of hydroxide ion or in the presence of one millimole of hydroxide after a short induction period. This seems to indicate that the metallated dye complex is unstable in acid solution. The second millimole of hydroxide ion produced a neutral solution which faded very little. The next two millimoles of hydroxide ion per millimole of complex produced initial fading which soon leveled off to a stable color. The addition of further hydroxide ion continued the fading to colorless solutions.

These observations are in line with observations made on the *o,o'*-dihydroxyazobenzene[2] in which a complex containing five groups was indicated. The fading reaction, which occurs when the third and fourth hydroxide ion enter the coördination sphere, may be due to a difference in absorption characteristics of the new complex. The replacement of solvent molecules in the fourth and fifth coördination position of the copper(II) ion by hydroxide ions seems to give a copper(II)-dye-dihydroxy complex.

Such change in color upon substituting more than four groups in the copper coördination sphere was observed by Bjerrum.[8] It is also in line with the observations of Jonassen, LeBlanc and Rogan in copper(II) amine complexes.[9]

Acknowledgment.—The financial support of the Research Corporation for part of this work is gratefully acknowledged.

NEW ORLEANS, LOUISIANA

---

[7] A. Burawoy, *et al.*, *J. Chem. Soc.*, 4793 (1952).

[8] J. Bjerrum and J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[9] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, THIS JOURNAL, **72**, 4968 (1950).