topic composition of the water was established by equilibrating it with CO_2 and analyzing the CO_2 by means of a mass spectrometer. The second experiment differed only in that the reactant solution and the reagents needed to precipitate the double salt were not precooled before being added.

The results obtained are presented in Table I.

TABLE I

TRACER EXPERIMENTS ON THE AQUATION OF $Co(NH_3)_5CO_3^+$ IN ACID

	$N_{obsd.}$ in water from ion	$N_{calcd.}$ for H_2O from solvent
Experiment 1	2.197×10^{-3}	7.90×10^{-3}
Experiment 2	2.630×10^{-3}	7.52×10^{-3}
Blank; reaction in unenriched H_2O	2.158×10^{-3}	....

The result obtained in Expt. 1 is very close to that in the blank. The higher value in Expt. 2 can be attributed to the exchange[8] of $Co(NH_3)_5H_2O^{+++}$ with H_2O^* which took place when the solution warmed as the precipitating agents were added.

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[8] This exchange is at present under study (A. C. R. and H. T.). The method for isotopic sampling will be described in more detail when the data on the exchange are presented for publication.

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Spectrophotometry of Ferric Chloride Complexes with *m*-Cresol, Salicylaldehyde and Ethyl Acetoacetate

BY RALPH L. HERBST, JR., ROBERT H. CLOSE, FRANK J. MAZZACUA AND ROBERT F. DWYER

In 1934, the structure $Fe(OR)_6^{---}$, where OR represents the phenoxide or enolate ion, was postulated by Wesp and Brode[1] for the colored complex formed in the reaction of ferric chloride with phenols and enols. This postulation was based on the observation that the ferric chloride–phenol complexes gave absorption spectra similar to that found for the iron(III) ion–cyanate and monothiocyanate iron(III) ion complexes. At this time these latter complexes were described as $Fe(CN)_6^{---}$ and $Fe(CNS)_6^{---}$, respectively. More recent investigations by Bent and French,[2] Edmonds and Birnbaum,[3] and Vosburgh and associates[4] have shown the monothiocyanate iron(III) complex to be $Fe(SCN)^{++}$. These results prompted a study of the iron(III) ion–phenol and enol complexes by the method of continuous variations employed by Vosburgh.[4]

Experimental

Materials.—All the organic compounds were freshly distilled: *m*-cresol, b.p. 201°; salicylaldehyde, b.p. 196.5°; ethyl acetoacetate, b.p. 180°; reagent grade $FeCl_3 \cdot 6H_2O$ was used.

Method.—The experimental details have been described by Vssburgh.[4] For *m*-cresol and ethyl acetoacetate, the mixtures were made up by volume from a freshly prepared stock solution of 0.02003 *N* ferric chloride and a 0.02003 *M* stock solution of the organic compound. In the case of salicylaldehyde, it was necessary to use more dilute stock solutions of 0.0001 *M*. Optical densities were measured with a Beckman model B spectrophotometer within 10–15 minutes after the mixtures were prepared. Preliminary scanning of 1:1, 1:3 and 1:6 mixtures of ferric chloride–*m*-cresol, ferric chloride–salicylaldehyde, and ferric chloride–ethyl acetoacetate between 400 and 675 mμ showed that only one colored compound formed in each case since curves of the same shape resulted. Next a series of mixtures was measured at four arbitrarily selected wave lengths. The values of *y*, the difference between the optical density observed and the corresponding optical density calculated for no reaction, were plotted *versus x*, the volume of the phenol or ester solution added to the volume $(1 - x)$ of the ferric chloride solution. The data are plotted in Figs. 1 and 2; the *y* terms have been multiplied by constants for clarity in presentation. The optical density of the blank ferric chloride solution showed no change within the time the measurements were made.

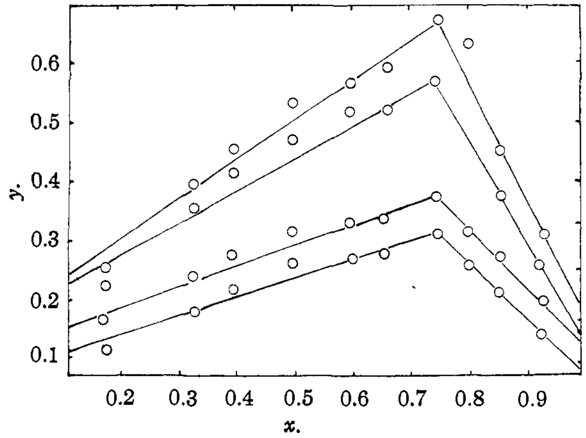

Fig. 1.—Ferric chloride-ethyl acetoacetate from top to bottom: 520, 475, 510, 490 mμ.

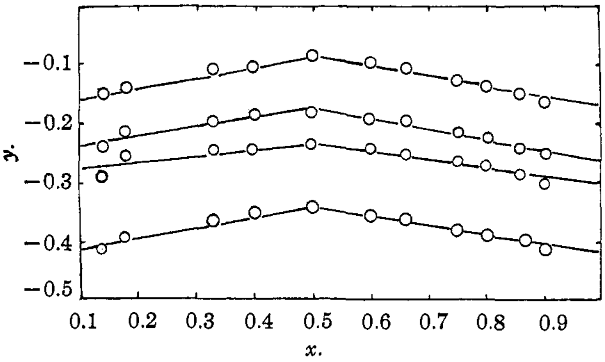

Fig. 2.—Ferric chloride–salicylaldehyde from top to bottom: 540, 520, 500, 560 mμ.

Results and Discussion

As shown in Figs. 1 and 2, the maxima for the colors occurred at 1 ferric chloride:3 ethyl acetoacetate and at a 1:1 ratio for ferric chloride–salicylaldehyde. A similar plot has also shown that the maximum occurs at 1 ferric chloride:3 *m*-cresol. At optical density readings of 0.704, 0.242 and 0.341 for ethyl acetoacetate, salicyladehyde and *m*-cresol, these maxima occurred at 510, 500 and 525 mμ, respectively Thus under the conditions used only one complex occurred for each pair of

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[1] E. F. Wesp and W. R. Brode, THIS JOURNAL, **56**, 1037 (1934).

[2] H. B. Bent and C. L. French, *ibid.*, **63**, 568 (1941).

[3] S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

[4] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941); R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1631 (1942).

compounds and no evidence was found for Fe(OR)$_6^{---}$. It is possible that other maxima might be observed at different concentrations and wave lengths. For ethyl acetoacetate, the ferric chloride is believed to react with the cis enol form.[5] Letellier[6] has reported that the maximum of color exists at the ratio of 1 ferric chloride:2 ester in water. The existence of other complex ions has been demonstrated.[7]

The concentration of OR ions may be an important factor in determining which particular complex is formed.[1] It is of interest, therefore, to compare the ionization constants of the organic compounds used. The classical dissociation constants in water at 25° for salicylaldehyde and *m*-cresol are 1.53×10^{-5} [8] and 0.98×10^{-10},[9] respectively. Using the relationship[10]

$$K_a = K_g(1 + K_E)/K_E \qquad (1)$$

where K_a is the classical dissociation constant of the enol form, K_g is the classical dissociation constant, and K_E is the enol–keto equilibrium constant results in a value of 2.9×10^{-10} for K_a for ethyl acetoacetate in water at 25°. Values of 2.09×10^{-11} [10] for K_g and 0.078[5] for K_E were used. Thus it is the more acidic compound, salicylaldehyde, which forms the 1:1 complex. This may be due to steric influences between the ortho CHO group and the hydrated ferric ion.

In regard to electrolysis experiments, Wesp and Brode[1] reported that the phenol complex migrates toward the cathode, while Bent and French[2] claim the color migrates toward the anode. Our results show that the complexes for *m*-cresol and ethyl acetoacetate are neutral; the salicylaldehyde complex should migrate toward the cathode. The observed disappearance of color may be due to the instability of the complex. Due to the neutral nature of the *m*-cresol and ethyl acetoacetate complexes it is essential to establish the existence of the RO$^-$ complex rather than a possible ROH complex. A determination of the *p*H of the solutions as the complexes are formed may prove fruitful in establishing this fact.

Acknowledgment.—The authors are indebted to Mr. Joseph M. Rizzo for technical assistance.

[5] H. Henecka, *Chem. Ber.*, **81**, 179 (1948).

[6] L. Letellier, *Bull. Sci. Pharmacol.*, **38**, 145–217 (1931).

[7] B. Emmert and W. Seebode, *Ber.*, **71B**, 242 (1938).

[8] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 6, 1929, p. 279.

[9] D. R. Boyd, *J. Chem. Soc.*, 1540 (1915).

[10] M. L. Eidinoff, This Journal, **67**, 2072 (1945).

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Cevine, a Correction

By Léo Marion, D. A. Ramsay and R. Norman Jones

In a previous study of the infrared absorption spectra of a number of alkaloids[1] we reported the presence of a carbonyl absorption band in the infrared spectrum of cevine and concluded that this alkaloid contained a carbonyl group. At the suggestion of Dr. H. L. Holmes we re-examined the base on which our observation had been made and found that it consisted not of cevine but of one of the minor alkaloids occurring with it. This alkaloid which is obtained like cevine by saponification of crude veratrine, crystallizes in short prismatic needles melting at 266–270.5° whereas cevine melts at 164–174°. The infrared absorption spectrum of an authentic sample of cevine *does not* contain a carbonyl absorption band.

[1] L. Marion, D. A. Ramsay and R. N. Jones, This Journal, **73**, 305 (1951).

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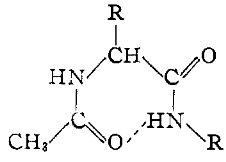
Additional Studies on the Intramolecular Hydrogen Bonding in Acetylglycine N-Methylamide

By San-ichiro Mizushima, Takehiko Shimanouchi, Masamichi Tsuboi and Reisuke Souda

In a previous paper[1] we reported our experimental results of near infrared absorption observed for $CH_3CONHCHRCONHCH_3$ and $CH_3CONHCHRCONHC_6H_5$ (R = H or C_4H_9) in dilute carbon tetrachloride solutions. All these compounds show two NH bands at about 2.9 μ and 3.0 μ of which the former is assigned to the vibrations of the NH group in the free state and the latter to that involved in the *intramolecular* hydrogen bonding of the structure



which corresponds to "B form" (one of the two unit structures of a polypeptide chain) proposed by us in 1947.[2] In view of the importance of proving the existence of B form in the structural chemistry of proteins we have recently made additional measurements of the near infrared absorption, the results of which will be reported in the present note.

In order to obtain further information concerning the relation between molar absorption coefficient κ and concentration *c* for these two NH bands measurements were made at 60° on carbon tetrachloride solutions of acetylglycine N-methylamide $CH_3CONHCH_2CONHCH_3$ of different concentrations *c* and absorption path-lengths *l*, keeping the product $c \times l$ constant. The results are shown in Fig. 1. If these two NH bands arise solely from single molecules and not from associated molecules (*intermolecular* hydrogen bonding), all the curves (1), (2) and (3) of Fig. 1 must be of the same form. Actually they are found almost of the same form, but differ slightly from one another.

Let us now consider to what extent these three absorption curves should differ from one another, if the 2.98 μ band were to be assigned solely to the *intermolecularly* hydrogen-bonded NH vibration (*i.e.*, solely to the NH association band). Since

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[2] T. Shimanouchi and S. Mizushima, *Kagaku*, **17**, 24, 52 (1947); *Bull. Chem. Soc. Japan*, **21**, 1 (1948), see *C. A.*, **43**, 8843 (1949).