Physico-chemical Studies of the Co(II)-succinimide Complex in Aqueous Medium

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With 6 Figures

Summary

Spectrophotometric, conductometric, pH-metric studies of Cobalt(II) succinimide system gave the formation of 1:2 complex in alkaline media. The studies were carried out in aqueous medium. The stability constant as determined by JOB's method of continuous variation was $2.4 \cdot 10^5$.

The biuret reaction of imides in the ammoniacal, ethanolic and pyridine media have been carried out[1]). LEY and WERNER[2]) reported the hydrolytic nature of the succinimide complex of copper. LAMBI[3]) studied the magnetic properties of complex derivatives of succinimide with iron, nickel and cobalt. These studies were confined to the study of the interaction of these heavy metals with succinimide in non-aqueous media; no attempt, however, seems to have been made to study these systems in aqueous medium and determine the nature and composition of these complexes Investigation in this direction was therefore undertaken employing various physico-chemical methods to establish the composition of the complex.

Experimental

Reagents: Cobaltous acetate used was of Reidel Analar grade. Succinimide (m.p. 124 °C) was prepared by the method (Practical Organic Chemistry by A. I. VOGEL, 1961, p. 840). Potassium hydroxide used was also of Analar quality.

Solutions: All the solutions were prepared in double distilled water. The solution of cobaltous acetate was standardised by gravimetric method (Quantitative Inorganic Analysis by A. I. VOGEL, 1961, p. 528). The solution of succinimide was prepared in one equivalent potassium hydroxide.

[1]) TSCHUGAEFF, Ber. dtsch. chem. Ges. **38**, 2899 (1905).

[2]) M. LEY and F. WERNER, Ber. dtsch. chem. Ges. **46**, 4040 (1913).

[3]) LAMBI and TREMOLADA, Gazz. chim. Ital. **65**, 322 (1935).

Apparatus: Optical density measurements were carried out with the help of 'Bausch and Lombs' spectronic-20.

Conductance measurements were carried out by conductivity Bridge type CL 01/01 A model.

For pH-metric titrations, Cambridge pH-meter was employed.

Results and discussion

Preliminary experiments showed that:

1. There was no reaction on mixing both the reactants without the addition of one equivalent potassium hydroxide corresponding to succinimide.

2. When cobaltous acetate was allowed to react with succinimide, prepared in one equivalent potassium hydroxide, a dark blue colour was developed and within few minutes blue precipitate, settled down if higher concentration of succinimide is employed.

Optimum pH for the formation of the complex

In order to verify whether hydrogen ions were liberated during complex ion formation, pH-metric titrations of the mixtures of cobaltous acetate and succinimide in the ratio 1:0; 1:1; 1:2 and 0:2 against 0.099 M KOH were made (Fig. 1). Since the down-word shift in pH was observed above

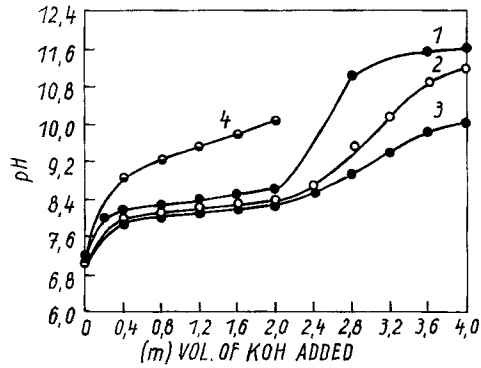


Fig. 1.
Curve 1: 5.0 ml Co(II) Acetate (0.02 M) + 10.0 ml water titrated with KOH (0.099 M); Curve 2: 5.0 ml Co(II) acetate + 5.0 ml succinimide (0.02 M) + 5cc water with KOH (0.099 M); Curve 3: 5.0 ml Co(II) acetate + 10 ml succinimide with KOH (0.099 M); Curve 4: 10.0 ml succinimide 0.02 M) + 5 cc water with KOH (0.099 M)

pH 8.64, it was concluded that the formation of the complex would take place above this pH. Blank experiments were performed separately with succinimide and caustic potash solutions. The curves obtained therein did not interfere with the titration curves described above. Fig. 1, curve II for the pH-metric titration of cobaltous acetate with caustic potash in presence of one mole of succinimide shows an inflextion at m = 2.2 ml. indicating the formation of 1:2 derivative corresponding to metal and ligand.

pH-metric and conductometric titrations

pH-metric (Fig. 2) and conductometric titrations (Fig. 3) were carried out in presence of one equivalent KOH corresponding to succinimide to establish the composition of the reaction product. The ratio obtained by both the methods was 1:2 corresponding to Co(II): succinimide.

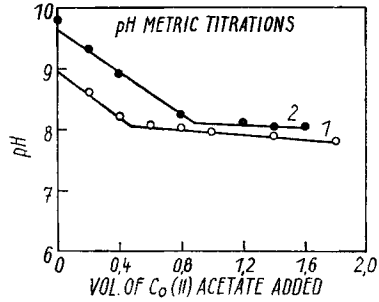


Fig. 2. Curve 1: 10.0 ml succinimide (0.01 M) titrated with Co(II) acetate (0.1 M); Curve 2: 20.0 ml succinimide (0.1 M) titrated with Co(II) acetate (0.1 M)

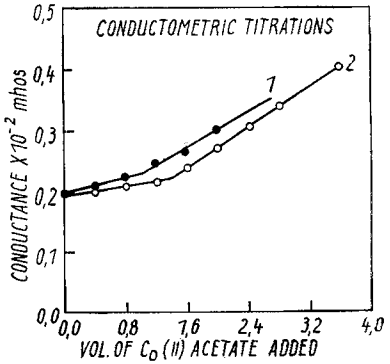


Fig. 3. Curve 1: 20.0 ml of succinimide (0.01 M) titrated with (0.1 M) Co(II) acetate; Curve 2: 30.0 ml of succinimide (0,01 M) titratedwith (0.1 M) Co(II)acetate

Spectrophotometric studies

The results obtained by pH-metric and conductometric titrations were also confirmed by spectrophotometric studies. Since in the solutions containing higher concentration of succinimide, the precipitate occurred after 8 or 10 minutes, the O.D. measurements were made just after mixing the solutions.

Vosburgh Copper's method was employed for knowing the number of complexes formed. 0.025 M of the two reactants (succinimide in one equivalent KOH) were mixed in the molar ratios 1:3, 1:2, 1:1, 2:1, 3:1 and optimal densities measured in wavelength region 380 to 800 mμ. The plot of O.D. against wavelength gave a sharp maxima at 630 mμ thereby showing the existence of only one complex. (The mixture of cobaltous acetate and water gave the maxima at 500 mμ.) The composition of the complex was determined employing Job's method of continuous variation[4]), molar ratio method[5]) and slope ratio method[6]). Measurements were made at 625, 630 and 635 mμ.

[4]) Compt. rend **180**, 928 (1925); Ann. Chim. **X, 9,** 113 (1928).

[5]) Idem, ibid. **36**, 285 (1959).

[6]) Harvey and Manning, J. Amer. chem. Soc. **72**, 4488 (1950); **74**, 4744 (1952).

BEER's law

Under the conditions mentioned above, the absorption of the cobaltous complex at 630 and 635 mμ obeys BEER's law for the range tested (00 to 116 ppm) Fig. 4. To evaluate optimum ranges and analytical accuracy, RINGBOM's Curve[7]) was drawn by plotting % absorbance as ordinate against log concentration as abscissa. Thus the optimum concentration with the highest accuracy ranges was from 16 ppm to 80 ppm (Fig. 5).

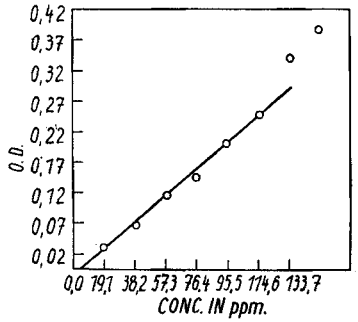


Fig. 4.

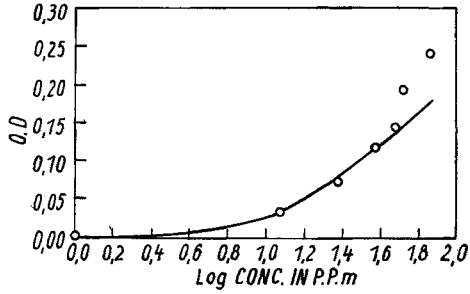


Fig. 5.

Effect of diverse anions

The effect of different anions on the formation of complex was studied. A difference of more than 0.01 in absorbance unit was taken as an interference. The anions which have been found to interfere in the estimation of cobalt(II) with succinimide were sulphate, bisulphate, oxalate and bromide while that of nitrate, chloride chlorate, persulphate, carbonate did not interfere.

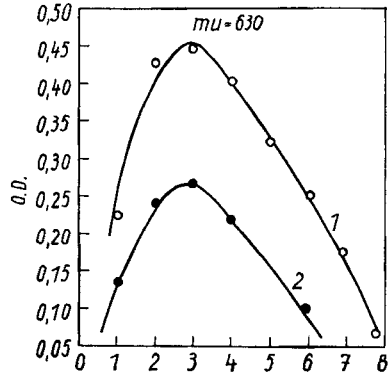
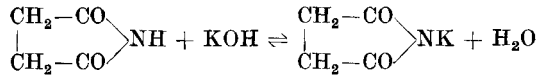
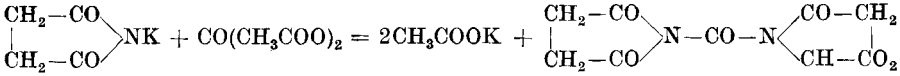


Fig. 6.
Vol. of cobaltous acetate (0.02 M) added curve(1); vol. of cobaltous acetate (0.01 M) added curve(2)

[7]) Z. RINGBOM, Z. analyt. Chem. **115**, 332 (1938/39).

The ratio as obtained by all the physico-chemical methods was 1:2 corresponding to the cobalt (II) and succinimide. The stochiometric reaction may be represented by the following equation.





The stability constant of this complex was determined by JOB's method of continuous variation (Fig. 6) which was found to be $2.4 \cdot 10^5$.

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