Am Myn

THIS DOCUMENT CONSISTS OF 8 PAGES
THIS IS COPY 4 OF 107

UNCLASSIFIED

MM-105

Contract Number AT-33-1-GEN-53

MONSANTO CHEMICAL COMPANY - UNIT III

DAYTON, OHIO

RECEIVED
OCT 11 1995
OSTI

M. M. Haring
Laboratory Director

THE IDENTIFICATION OF COMPLEX IONS IN SOLUTION BY
SPECTROPHOTOMETRIC MEASUREMENTS
(Information Report)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Date: May 18, 1948

Prepared by: R. A. Staniforth

Distributed: MAY 21 1948

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISTRIBUTION

1. - M. M. Haring
2. - R. A. Staniforth
3. - J. H. Payne, Jr.
4. - Area Manager
5. - Area Manager
6. - Area Manager
7. - Central Files
8. - Central Files
9. - Central Files
10. - Central Files

INTRODUCTION

A method for the identification of compounds formed in solutions by reaction of two components has been described by Job².

2 - Job, Ann. chim., (10) 9, 113 (1928)

The method is applicable to complex ions. The formation of many complex ions can be represented by the equation

in which A is a metallic ion and B may be either a molecule like ammonia or an anion. To determine n, solutions of A and B of the same molar concentration are mixed in varying proportions, and a suitable property of the resulting solutions is measured. The difference (Y) between each value found and the corresponding value of the property calculated for no reaction is plotted against the composition. The resulting curve (Y against composition) should have a maximum if the property measured has a larger value for the complex ion than for A or B, or a minimum if smaller. Job has shown that the composition at which the difference Y is a maximum bears a simple relation to n of Equation (above) and is independent of the equilibrium constant. This method has been called the method of continuous variations.

If the molar concentrations of the solutions of A and B are not the same, the position of the maximum in the curve is a function of the equilibrium constant as well as of n. If n is known and the stability of the complex ion not too great, the equilibrium constant can be determined.

The absorption of monochromatic light is a suitable property for this method, because complex ions are often differently colored from their components. Also, the absorption of light is proportional to the concentration of the absorbing species, which is one of the necessary conditions.

The method of continuous variations would be more useful if it could be readily ascertained in any particular case whether or not more than one compound is formed from a pair of components. It was also of interest to see what use, if any, could be made of the method when more than one complex ion is formed from the same components.

THEORETICALCase IConditions

1. Substances A and B react according to the equation:

2. A and AB_n are ions of the same valence type, and B is a non-electrolyte. This condition is necessary in order that activity coefficients be unnecessary (in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength).

3. If it can be shown that the activity coefficients do not change appreciably even though the constant ionic strength condition is not attained, the following derivation will hold at least approximately.

Derivation

The solutions of A and B, both of concentration M moles per liter, are mixed in varying proportions.

Let the mixtures be made by the addition of x liter of B to (1 - x) liter of A ($x < 1$), with no appreciable volume change on mixing.

Let c_1 , c_2 , and c_3 be the concentrations of A, B and AB_n respectively at equilibrium. Hence

$$c_1 \quad c_2 \quad c_3 \quad \text{equilibrium}$$

$$M(1-x) \quad Mx \quad 0 \quad \text{initial}$$

For any mixture the following equations apply

$$2. \quad c_1 = M(1-x) - c_3$$

$$3. \quad c_2 = Mx - nc_3$$

$$4. \quad K = \frac{c_1 c_2^n}{c_3}$$

The condition for a maximum in the curve of c_3 plotted against x is that

$$5. \quad \frac{dc_3}{dx} = 0$$

Differentiation of Equations 2, 3, and 4 and combination of the three resulting differential equations with Equations 2, 3, 4, and 5 is as follows:

$$6. \quad \frac{dc_1}{dx} = -M - \frac{dc_3}{dx} \quad \text{diff. of (2)}$$

$$7. \quad \frac{dc_2}{dx} = M - n \frac{dc_3}{dx} \quad \text{diff. of (3)}$$

$$8. \quad K \frac{dc_3}{dx} = c_2^n \frac{dc_1}{dx} + c_1 n c_2^{n-1} \frac{dc_2}{dx} \quad \text{diff. of (4)}$$

$$9. \quad 0 = -c_2^n M + n c_1^{n-1} M \quad \text{comb. of (6), (7), and (8)}$$

$$10. \quad 1 = n c_1 c_2^{-1} = n \frac{c_1}{c_2} \quad \text{simplification of (9)}$$

$$11. \quad 1 = n \frac{M - xM - c_3}{xM - n c_3} = \frac{nM - nxM - n c_3}{xM - n c_3} \quad \text{substitution of (2), (3) in 10}$$

$$12. \quad xM - n c_3 = xM - nxM - n c_3$$

$$13. \quad x = n(1-x)$$

$$14. \quad n = \frac{x}{(1-x)}$$

It remains to be shown that a maximum (or minimum) in the absorption of monochromatic light when x is varied coincides with the maximum of c_3 . It will be recalled that the general absorption law (Bouguer-Beer) may be expressed:

$$15. -\log T = \log \frac{I_0}{I} = kcb = D$$

where

T = transmittancy (100 T = per cent transmittancy)

I_0 = intensity of incident radiation

I = intensity of emergent radiation

k = extinction coefficient

c = concentration of absorber

b = thickness of absorber

D = optical density

Now, if k_1 , k_2 , and k_3 are the extinction coefficients of A, B, and AB_n at a given wave length, the optical density, D , is

$$16. D = b(k_1 c_1 + k_2 c_2 + k_3 c_3)$$

Let Y be the difference between D of Equation 16 and the optical density that the solution would have had if there had been no reaction on mixing the solutions of A and B.

$$17. Y = b \left[k_1 c_1 + k_2 c_2 + k_3 c_3 - k_1 M(1-x) - k_2 Mx \right]$$

Differentiate Equation 17 with respect to x

$$18. \frac{dY}{dx} = b \left[k_1 \frac{dc_1}{dx} + k_2 \frac{dc_2}{dx} + k_3 \frac{dc_3}{dx} + k_1 M - k_2 M \right]$$

Substituting (6) and (7) in (18)

$$19. \frac{dY}{dx} = b \left[-k_1 M - k_1 \frac{dc_3}{dx} + k_2 M - k_2 n \frac{dc_3}{dx} + k_3 \frac{dc_3}{dx} + k_1 M - k_2 M \right]$$

Simplifying

$$20. \frac{dY}{dx} = b \left[k_3 - k_1 - k_2 n \right] \frac{dc_3}{dx}$$

Differentiating with respect to x

$$21. \frac{d^2 Y}{dx^2} = b \left[k_3 - k_1 - k_2 n \right] \frac{d^2 c_3}{dx^2}$$

From Equations (20) and (21) the following conditions can be seen necessary:

Y a maximum

$$a. \frac{dY}{dx} = 0$$

$$b. \frac{d^2 Y}{dx^2} \text{ negative}$$

to attain (a) and (b)

$$c. \frac{dc_3}{dx} = 0$$

c₃ a maximum

$$d. \frac{d^2 c_3}{dx^2} \text{ negative}$$

$$e. k_3 > k_1 + k_2 n$$

or

$$f. k_3 > k_1 \text{ if } k_2, \text{ the extinction}$$

coefficient of compound B is assumed to be zero which is often true in complex ion formation.

Y a minimum

$$a. \frac{dY}{dx} = 0$$

$$b. \frac{d^2 Y}{dx^2} \text{ positive}$$

to attain (a) and (b)

$$c. \frac{dc_3}{dx} = 0$$

$$d. \frac{d^2 c_3}{dx^2} \quad \begin{array}{l} c_3 \text{ a maximum} \\ \hline \text{negative} \end{array}$$

$$e. k_3 < k_1 + k_2 n$$

or simplify

$$f. k_3 < k_1$$

Thus, a determination of the value of x for which c_3 is a maximum allows the calculation of n by Equation 14.

RAS/rcc

/