

CHAPTER 2.

INDIRECT DETERMINATION OF EQUILIBRIUM CONSTANTS

It is evident from the previous chapter that the aqueous solution of acetic acid is a mixture of few species existing in equilibrium namely cyclic dimers, linear dimers, linear polymers, and free ions the extent of which depends on the concentration of acetic acid solution. It follows then that each of the equilibrium constants for the formation of cyclic dimers, linear dimers, and linear polymers is the function of the mole fraction of that species as well as the counterspecies. If the relation of these equilibrium constants and the fraction of protons of the species groups are known concurrently with the fraction of protons of H_2O and H^+ , the above set of equilibrium constants can be found.

In the work reported here, NMR spectroscopic method was employed since it can respond to and record of any protonic changes in the solution undertest. The results of the NMR spectroscopy usually are expressed as the chemical shift, δ . In this work the aqueous solutions of acetic acid are used and the chemical shift of ionising proton, $\delta(\text{H}^+)$ are the desired quantity to accomplish the calculation. Unfortunately, this quantity cannot be directly determined from such a weak acid as acetic acid. The indirect method is therefore developed whereby the desired value, $\delta(\text{H}^+)$ is obtained. The remaining of this chapter is devoted to the presentation of the developments of some equations necessary for the computation of the equilibrium

constants for the formation of cyclic dimer, linear dimers and linear polymers in acetic acid solution.

2.1 The relation between the chemical shift of hydrogen ions and the average chemical shift of aqueous hydrochloric acid

In 1953, Gutowsky and Saika⁽¹⁹⁾ reported their work on the dissociation, chemical exchange and the proton magnetic resonance in some aqueous electrolytes e.g. HOAc, HCl, HClO₄ and HNO₃ using the NMR technique. For HOAc, they took into account only the presence of monomer. The position of the proton resonance was determined by averaging of the absorption over the two chemical states i.e. proton in monomer and in water. Consequently they showed that the chemical shift was given by

$$\delta = p_1 \delta_{\text{HOAc}} + p_2 \delta_{\text{H}_2\text{O}} \quad (2.1)$$

In the case of strong electrolyte such as dilute hydrochloric acid, where complete dissociation was assumed they showed that the position of the proton resonance in term of the chemical shift was similar to that of acetic acid. Hence, eq(2.1) is adopted in this work with some modification in order to accommodate other species as well as monomer. The modified form is as follows.

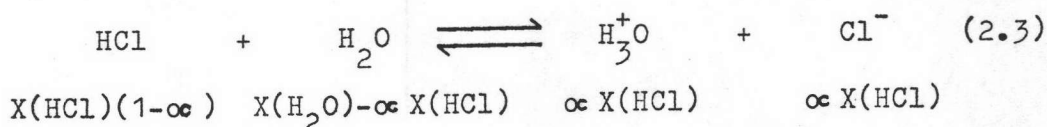
$$\delta(\text{HCl}) = f(1)\delta(\text{H}_3\text{O}^+) + f(2)\delta(\text{H}_2\text{O}) \quad (2.2)$$

where

$\delta(\text{HCl})$ is an average chemical shift of aqueous hydrochloric acid. $\delta(\text{H}_3\text{O}^+)$ is the chemical shift of hydronium ions.

$f(1)$ and $f(2)$ are the fraction of protons as hydronium ions and water protons respectively.

It is customary to represent schematically the equilibrium in aqueous solution of hydrochloric acid as.



where $X(\text{HCl})$ and $X(\text{H}_2\text{O})$ are the stoichiometric mole fractions of hydrochloric acid and water respectively, and α is an apparent degree of dissociation. If complete dissociation is assumed, that is $X(\text{H}_2\text{O}) \gg X(\text{HCl})$ then the position of the proton resonance can be determined by averaging chemical shift in the same manner as given in eq(2.2). Thus by making $f(2) = 1-f(1)$ and assuming the complete dissociation, the equation below is obtained.

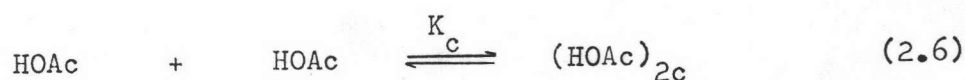
$$\delta(\text{HCl}) - \delta(\text{H}_2\text{O}) = [\delta(\text{H}_3\text{O}^+) - \delta(\text{H}_2\text{O})] f(1) \quad (2.4)$$

A plot of $\delta(\text{HCl}) - \delta(\text{H}_2\text{O})$ against $f(1)$ yields a straight line with $\delta(\text{H}_3\text{O}^+) - \delta(\text{H}_2\text{O})$ as its slope from which $\delta(\text{H}_3\text{O}^+)$ can be evaluated. Since $\delta(\text{H}_2\text{O})$ is determinable, it is obvious that the chemical shift of hydrogen ions, $\delta(\text{H}^+)$ can simply be calculated from the relationship below.

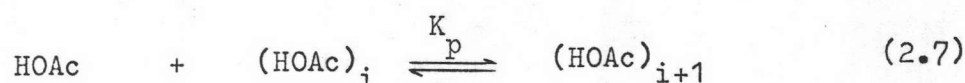
$$\delta(\text{H}^+) = 3\delta(\text{H}_3\text{O}^+) - 2\delta(\text{H}_2\text{O}) \quad (2.5)$$

2.2 The theory of the weight average for acetic acid-water system

The existence of monomers, cyclic dimers and chain polymers can be represented simply by two equilibrium processes.



and



The first equilibrium indicates the formation of a cyclic dimer from two monomeric acid units and the second shows the addition of a monomer unit to an existing polymer of i units to form $i+1$ unit polymer.

The use of a single equilibrium constant for all polymer growth equilibria is not adequate since it has been shown^(20,21) that the equilibrium constant for two monomer bonding together to form a linear dimer should be different from that for a monomer adding to an n -mer ($n \geq 2$). Therefore, the equilibrium constants for the above reactions should be in the forms

$$K_c = \frac{[(\text{HOAc})_{2c}]}{[\text{HOAc}]^2} = \frac{X_c}{X_1^2} \quad (2.8)$$

$$K_1 = \frac{[\text{HOAc-HOAc}]}{[\text{HOAc}]^2} = \frac{X_2}{X_1^2} \quad (2.9)$$

$$K = \frac{[(\text{HOAc})_{i+1}]}{[(\text{HOAc})_i] [\text{HOAc}]} = \frac{X_{i+1}}{X_i X_1} \quad (2.10)$$

where

K_c is the equilibrium constant for the formation of a cyclic dimer, $(\text{HOAc})_{2c}$ from two monomeric acid units, HOAc.

K_1 is the equilibrium constant for the formation of a linear dimer, HOAc-HOAc from two monomeric acid units.

K is the equilibrium constant for the formation of a polymer of $i+1$ unit, $(\text{HOAc})_{i+1}$ from a polymer of i unit, $(\text{HOAc})_i$ and a monomeric acid unit.

X_c is the mole fraction of the cyclic dimer.

X_1 is the mole fraction of the monomer.

X_i is the mole fraction of the linear polymer of length i .

Expressions for the mole fraction of each of the constituents can be obtained in term of the mole fraction of the monomer by solving the set of simultaneous equilibrium expressions (2.8), (2.9) and (2.10), thus.

$$X_c = K_c X_1^2 \quad (2.11)$$

and

$$X_i = K_1 K^{i-2} X_1^i = (K_1/K^2)(KX_1)^i \quad (2.12)$$

(see Appendix 1)

In order to obtain an expression for X_1 in terms of the equilibrium constants, it is necessary to use a mass balance relationship for the total acetic acid in the solution. Such a relationship is simply represented as.

$$n_A/n_T = \sum_{i=1}^{\infty} (i)X_i + 2X_c + X_A \quad (2.13)$$

where n_A is the total number of acetic acid molecules in solution, n_T is the total mole of species present. From, eq(A3.4) of Appendix 3, then.

$$n_A/n_T = X_1 + \frac{K_1 Y^2 (2-Y)}{K^2 (1-Y)^2} + 2X_C + X_{A^-} \quad (2.14)$$

Since the sample is an aqueous solution, water must have some roles such that its mole fraction, $X_W = n_W/n_T$, has to be taken into consideration. By making use of the fact that the summation of the mole fraction of all species present together must equal to unity, and that $X_{A^-} = X_{H^+}$, together with the aid of eq(A2.2) of Appendix 2, the final form of X_W is.

$$X_W = n_W/n_T = 1 - X_C - X_1 - \frac{K_1 Y^2}{K^2 (1-Y)^2} - 2X_{A^-} \quad (2.15)$$

where $Y = KX_1$

By some mathematical manipulations of eqs(2.11) and (2.12), eq(2.16) is obtained as below.

$$\frac{n_A}{n_W + n_A} = \frac{KY(1-Y)^2 + 2K_C Y^2 (1-Y)^2 + K_1 Y^2 (2-Y) + X_{A^-} K^2 (1-Y)^2}{K^2 (1-Y)^2 + K_C Y^2 (1-Y)^2 + K_1 Y^2 - X_{A^-} K^2 (1-Y)^2} \quad (2.16)$$

Equation(2.16) yields a fourth-degree polynomial of Y in terms of the three equilibrium constants, K , K_1 , K_C and the mole fraction of acetic acid molecules, X_{AS} , which is equal to $n_A/(n_W + n_A)$, and the mole fraction of acetate ions, X_{A^-} (see Appendix 4) as shown.

$$\begin{aligned}
& \frac{Y^4 + ((4K_c + K_l - K) - 2K_c X_{AS} + ((K - 2K_c - K_l) X_{AS} + (K - 2K_c - K_l)) C_{\bar{A}}/\beta) Y^3 +}{(X_{AS}^{-2} + (X_{AS} + 1) C_{\bar{A}}/\beta) K_c} \\
& \frac{(2(K - K_c - K_l) + (K_c + K_l + K^2) X_{AS} + ((K_c + K_l - 2K - K^2) X_{AS} + (K_c + K_l - 2K - K^2)) C_{\bar{A}}/\beta) Y^2 -}{(X_{AS}^{-2} + (X_{AS} + 1) C_{\bar{A}}/\beta) K_c} \\
& \frac{(2K^2 X_{AS} + K - ((2K^2 + K) X_{AS} + (2K^2 + K)) C_{\bar{A}}/\beta) Y}{(X_{AS}^{-2} + (X_{AS} + 1) C_{\bar{A}}/\beta) K_c} + \frac{K^2 X_{AS} - (K^2 X_{AS} + K^2) C_{\bar{A}}/\beta}{(X_{AS}^{-2} + (X_{AS} + 1) C_{\bar{A}}/\beta) K_c} = 0 \quad (2.17)
\end{aligned}$$

If the equilibrium constants are known, the monomer concentration can be obtained by solving eq(2.17), the concentration of a cyclic dimer and a linear dimer can then be obtained from eqs (2.11) and (2.12). In order to accomplish this, it is necessary to have expressions for the fractions of the various types of protons which contribute to the chemical shift as can be seen from eq(2.18).

$$\delta = f(E)\delta(E) + f(I)\delta(I) + f(C)\delta(C) + f(H^+)\delta(H^+) + f(H_2O)\delta(H_2O) \quad (2.18)$$

where

δ is an average chemical shift of all species.

$\delta(E)$ is the chemical shift of end protons.

$\delta(I)$ is the chemical shift of internal hydrogen bonding protons.

$\delta(C)$ is the chemical shift of hydrogen-bonded protons in cyclic dimers.

$f(E)$ is the fraction of acid protons found on the chain polymer end.

$f(I)$ is the fraction of acid protons forming hydrogen

bond linkages in the chain polymers.

$f(C)$ is the fraction of hydrogen-bonded protons in cyclic dimer.

The two last terms are determinable. Other terms can be derived as follows.

$$f(E) = \frac{\sum_{i=1}^{\infty} X_i}{2X_c + \sum_{i=1}^{\infty} (i)X_i + 2X_w + X_{H^+}} \quad (2.19)$$

The application of eqs(2.11), (A2.2), (A3.2) and (A4.12), leads to.

$$f(E) = \frac{KY + K_1 Y^2 / (1-Y)}{F(Y)} \quad (2.20)$$

where $F(Y) = 2K_c Y^2 + KY + K_1 Y^2 (2-Y) / (1-Y)^2 + 2K^2 (1-X_{AS}) +$

$$\frac{(K_c Y^3 - (K_c + K_1) Y^2 + (K - K^2) Y + K^2) C_{H^+} / \beta}{(1-Y)}$$

$$f(I) = \frac{\sum_{i=2}^{\infty} (i-1) X_i}{2X_c + \sum_{i=1}^{\infty} (i) X_i + 2X_w + X_{H^+}} \quad (2.21)$$

$$f(I) = \frac{K_1 Y^2 / (1-Y)^2}{F(Y)} \quad (2.22)$$

and

$$f(C) = \frac{2X_c}{2X_c + \sum_{i=1}^{\infty} (i) X_i + 2X_w + X_{H^+}} \quad (2.23)$$

$$f(C) = \frac{2K_c Y^2}{F(Y)} \quad (2.24)$$

Trial values for the equilibrium constants can now be solved from eq(2.17) which will give the value of Y ($Y = KX_1$). From the known value of Y one can proceed to evaluate f(E), f(I) and f(C) from eqs(2.20), (2.22) and (2.24) respectively. Nevertheless, eq(2.18) is still unsolved for δ if $\delta(E)$, $\delta(I)$ and $\delta(C)$ are not known. At this step, statistic principles are applied in order to get an average chemical shift at each acid concentration and fit the results with those obtained in the experiments. The procedure is described hereafter.

The non-linear least squares fit method is shown in eq(2.25) (in term of a standard deviation).

$$\sigma = \sqrt{\frac{\sum_{j=1}^N (\delta_j^{\text{obsd}} - \delta_j^{\text{calcd}})^2}{N-1}} \quad (2.25)$$

where

δ_j^{obsd} is the observed chemical shift for the j^{th} solution.

δ_j^{calcd} is the value calculated via eq(2.18) for the j^{th}

solution.

N is the number of acetic acid solution.

σ is a standard deviation of the NMR chemical shift.

$\delta(E)$, $\delta(I)$ and $\delta(C)$ are those values which minimize the value of σ . It is not possible to obtain an analytic expression for σ in terms of equilibrium constants, but, it is possible to obtain the least squares set of equilibrium constants by cyclising the above steps until the set of equilibrium constants with the smallest value of σ is found.

2.3 The application of equilibrium constants

Apart from what mentioned in 2.2, the equilibrium constants are also found useful for the calculation of mole percent of each equilibrium species in acetic acid solution. The procedure is shown stepwisely here. The macroscopic mole fraction of acetic acid, X_{MA} is defined as.

$$X_{MA} = \frac{\sum_{i=1}^{\infty} n_i + n_c + n_{A^-}}{\sum_{i=1}^{\infty} n_i + n_c + n_{A^-} + n_W} \quad (2.26)$$

X_{MA} can be obtained by making use of eqs (A2.2), (A4.11) and (2.26) and gives.

$$X_{MA} = \frac{X_1 + K_c X^2 + \frac{K_1 Y^2 + (K_c Y^3 - (K_c + K_1) Y^2 + (K - K^2) Y + K^2) C_{H^+} / \beta}{K^2 (1 - Y)}}{K^2 (1 - Y)} \quad (2.27)$$

The mole percent of each of the species can then be calculated.

$$\text{The mole percent} = \frac{100 X_{ES}}{X_{MA}} \quad (2.28)$$

Where X_{ES} is the mole fraction of a particular species which is calculated by eqs (2.11) and (2.12).