Dissociation Constant of Monochloro Acetic Acid by Emf measurements and related thermodynamic function

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ABSTRACT:- A number of workers have determined the dissociation constant of monochloroacetic acid using different methods, but there was variation in them. Therefore, the present work which is based on emf method is found to be more accurate and it was thought to recalculated the emf data of Wright measured from the cell.

Pt / QH, CH_2 Cl. CooH (M) Nacl (m) AgCl / Ag (&)

By applying modified Davies equation

$$\log \Upsilon_i = \frac{-AZ_i^2\sqrt{I}}{1+\sqrt{I}} \ Bi \ \mu$$

Where Bi, is additive parameter and reasonably independent of composition of ionic atmosphere unless there is drastic change in its composition. The recalculation was done at 0^0C and le was extrapolated against

$$\log \frac{[H^+][Cl \ CH_2 \ COO]}{[\ Cl \ CH_2 \ COOH]} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}$$

We have to also calculated transfer energetic from water to Chloroacetic acid media is calculating the thermodynamic parameter. They are $\Delta G^0_{transfer}$, $\Delta S^0_{transfer}$ and $\Delta H^0_{transfer}$. For the first step of deprotonation constant over calculated temperature and concentrated range have been carefully measured.

KEYWORDS:- Monochloroacetic acid , deprotonation constant, Thermodynamic quantity.

I.   INTRODUCTION:-

Monochloroacetic acid (MCA), is the organochlorine compound with the formula $ClCH_2COOH$. This carboxylic acid is a useful building- block in organic synthesis. In its largest scale application it is used to prepare the thickening agent Carboxymethyl cellulose and Carboxymethyl starch.

A study of the thermodynamic of a reaction in solution may read us to understand the properties of the solution better. The key to this study is the determination of PK of monochloroacetic acid then calculation of thermodynamic parameter. They are

$\Delta G^0 transfer, \Delta S^0 transfer$ and $\Delta H^0 transfer$

We therefore set up the cell like this

Pt, H_2 (g) Cl CH_2 COOH (M)   NaCl (m) AgCl Ag(S) ------------------------(G)
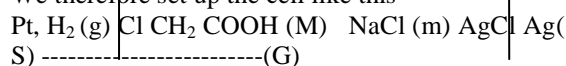
and described on the cell in present paper.

II.   EXPERIMENTAL:-

Doubly distilled monochloroacetic acid was taken and kept preserved in vacuum desiccator against moisture. Its purity was determined from time to time by titration from carbonate free base. Sodium Chloride (AR) was taken and dried at 128 C. A weighed amount of monochloroacetic acid and Sodium Chloride was transferred to weighed 500 ml measuring flask. It was then dissolved by adding doubly distilled water. When monochloro acetic acid Sodium Chloride completely dissolved by volume of the solution in the measuring flask was made up of mark. When it is attained the room temperature the measuring flask was weighed again. Buoyancy correction was done for all weighing and molality of NaCl (m) and CH_2 Cl COOH (m) where calculated.

The experimental solution were deoxygenated by passing nitrogen gas through the solution containing sintered glass delivery tube. Duplicates cells were set up for each solution from deoxygenated experimental solution. Electrodes were prepared by appropriate method and setting up the cell for measurement of emf. EMF value of the duplicate cells which agreed with one another within 0.10 MV.

III. RESULTS AND DISCUSSION:-

The Emf of the cell (C_1) is given by

$$E = E^0 - \frac{RT}{F} \ln m_{H^+.m_{Cl^- - \Upsilon H^+.\Upsilon Cl^-}}$$

$$= E^0 - \frac{2.30259 \ RT}{F}(\log m_H \ \ m_{Cl} + \log \Upsilon_H.\Upsilon_{Cl}$$

Here charge has been left for convenience and it will be followed henceforth.

Log m_H $.m_{Cl} = \frac{(E^0-E)F}{2.30259 \ RT} - \log \Upsilon_H.\Upsilon_{Cl}$

_____ (i)

where, Υ with the appropriate service subscript represent the activity coefficient.
Applying the equations

$$-\log \Upsilon i = \frac{AZ\, i^2 \sqrt{\mu}}{1+\sqrt{\mu}} - \beta_i\, \mu$$

For calculating $\log \Upsilon_H \Upsilon_{Cl}$ in equation (i), we get

$$\log m_H \cdot m_{Cl} = \frac{E^0 - E}{2.30259\,RT} + \frac{2\,A\sqrt{\mu}}{1+\sqrt{\mu}} \quad - \quad \beta \quad \sqrt{\mu}$$

—————————————————————————— (ii)
Where, $\beta = (\beta_H + \beta_{Cl})$

In equation (ii), E^0 is the standard potential of cell. The value of E^0 has been used as recommended by Harned and Ehlers[11]. (The value of A are taken as calculated by a Manov , Bates, Hamer and Acree[12].The value of a are taken as 0.4921, 0.4960, 0.5000, 0.5042, 0.5085, 0.5130, 0.5175, 0.5221 at 5^0, 10^0, 15^0, 20^0, 25^0, 30^0, 35^0 al 4^0 respectively.)

The value of $\frac{2.30259\,RT}{F}$ as taken as calculated by Bates[13].The β term is additive and is independent of the composition of ionic atmosphere at least up to $\mu = 0.01$ and the EMF accuracy is of the order of 0.1 mV provided drastic change in ionic atmosphere is not done.So the value of his cell (C1) containing a mixture of NaCl an Cl CH_2 COOH will be the same as in the cell given by Harned and Ehlers[11].
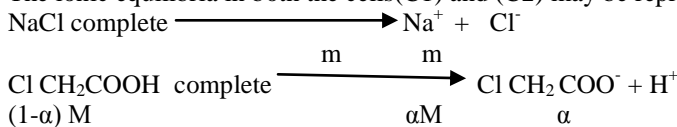The value of E^0 of quinhydrone has been used as recommended by Bates (taken Jves Book)[14] and the value of E^0 of Ag(s) ${}^{|}$AgCl at required temperature are known from the study of Harned and Ehlers (taken from and IVES book)[15] . The value of E^0 of the cell at various temperature are given in the table 1.

TABLE 1

Temp ^{0}C	E^0 of QH	E^0 of Ag\ AgCl, Cl$^-$	E^0 of Cell
5	0.71437	0.23400	0.48037
10	0.71073	0.23134	0.47939
15	0.70709	0.22854	0.47855
20	0.70343	022558	0.47785
25	0.69976	0.22246	0.47730
30	0.69607	0.21919	0.47688
35	0.69237	0.21570	0.47669
40	0.68865	0.21207	0.47658

The value of A&K are obtained from literature.
The ionic equilibria in both the cells(C1) and (C2) may be represented by
NaCl complete ————————➤ Na$^+$ + Cl$^-$
                                       m   m
Cl CH_2COOH complete ————————➤ Cl CH_2 COO$^-$ + H$^+$
(1-α) M   αM   α

Where, α is the degree of dissociation of monochloroacetic acid. Hence,
$m_{Na}{}^+ = m_{Cl}{}^- = m$
$m_H{}^+ = M_{Cl\,CH2COO}{}^- = \alpha\,M$ -- (iii)
$m_{Cl\,CH2COOH} = (1-\alpha)\,M$ -- (iv)

Now, $\mu = \frac{1}{2}\sum m_{zi^2}$
$= \frac{1}{2} m_{Na}{}_+ + \frac{1}{2} m_{Cl-} + \frac{1}{2} m_{H+} + \frac{1}{2} m_{Cl\,CH2COOH}{}^-$
$= \frac{1}{2}$ m $+ \frac{1}{2}$ m $+ \frac{1}{2}$ α M $+ \frac{1}{2}$ α M
$\mu=$ m + α M _____ (v)

In order to know the value of α and μ for any particular composition of the cell (m+ M)an arbitrary value m is assigned to μ. Knowing the value of μ , $m_H{}^+$ can be calculated from equation(ii) as $E^0 - E$, A, β and m_{Cl} are known.

From this value of m_H , β can be calculated from equation (v).`
Now a new valueof le can be found out from the equation (v) and with the help of α already calculated. This new value of μ is fed in equation (ii) the above process is repeated till μ is

constant up to sixth place of decimal. The value of α corresponding to the constant value of μ is taken to be correct and $m_{Cl\,CH2COO-}$, $m_H{}^+$, $m_{Cl\,CH2COOH}$ are obtained from the equation (ii) & (iv) .

The dissociation constant K of Cl CH $_2$ COOH is given by

$$K = \frac{a_H + \cdot a_{Cl\,CH2COO-}}{a_{ClCH2COOH}}$$

$$\frac{m_{H+} \cdot m_{Cl\,CH2COO-} \cdot \Upsilon_{H+} \cdot \Upsilon_{Cl\,CH2\,COO-}}{m_{CH2\,Cl.COOH} \cdot \Upsilon CH2Cl\,COOH}$$

log K = log $\frac{m_{H+} \cdot m_{ClCH\,2COO-}}{m_{CH2\,Cl\,COOH}}$ + log $\frac{\Upsilon H^+ \cdot \Upsilon CH2\,Cl.COO-}{\Upsilon CH2\,Cl.COOH}$

= log $\frac{m_{H+} \cdot m_{CH2\,Cl\,COO-}}{m_{CH2\,Cl\,COOH}}$ - $\frac{2\,A\sqrt{\mu}}{1+\sqrt{\mu}}$ + βμ

Or   log $\frac{m_{H+} \cdot m_{CH2\,Cl\,COO-}}{m_{CH2\,Cl\,COOH}}$ - - $\frac{2\,A\sqrt{\mu}}{1+\sqrt{\mu}}$ = logK -βμ -- (vi)

All the entities of LHS of equation (vi) for any particular cell solution are known. Therefore, LHS of equation (vi) can we found out from the particular cell solution. At any temperature a number of cells having different value of m &M where studied. The value of LHS of the equation (vi) where calculated and this value was plotted against μ, a straight line was obtained. The intercept at μ = 0 gave the value of log K and β was found from the slope of the line.

The value of K can also be obtained from the statistical method. It was found that the value of log K and β from statistical method are almost the same as obtained from the plotes of the points.
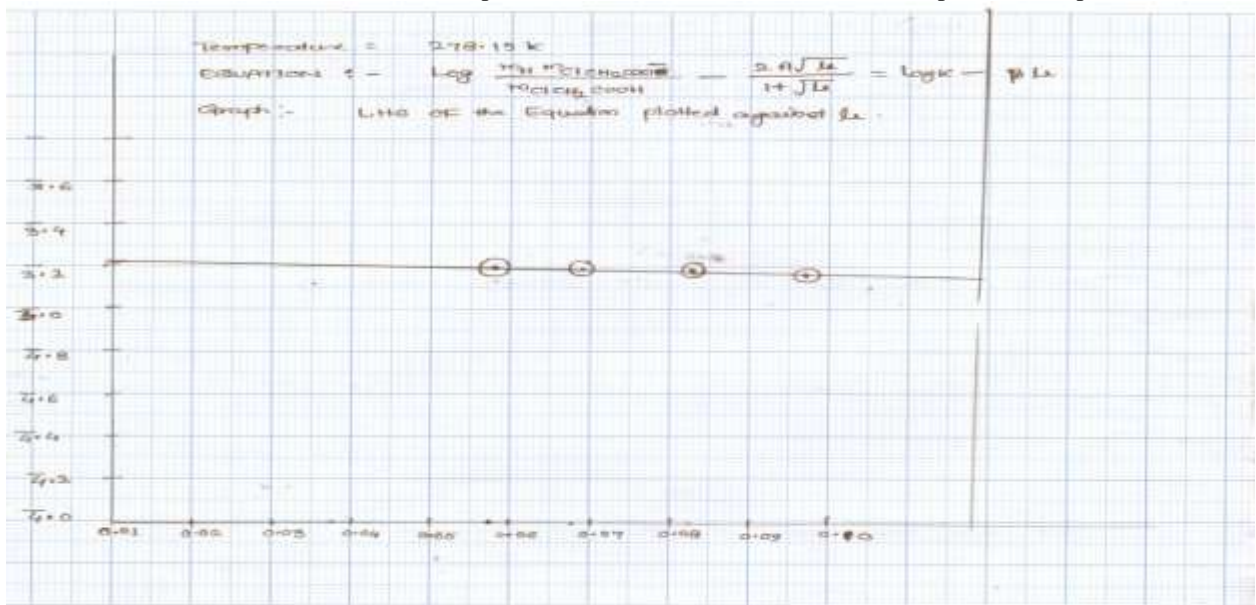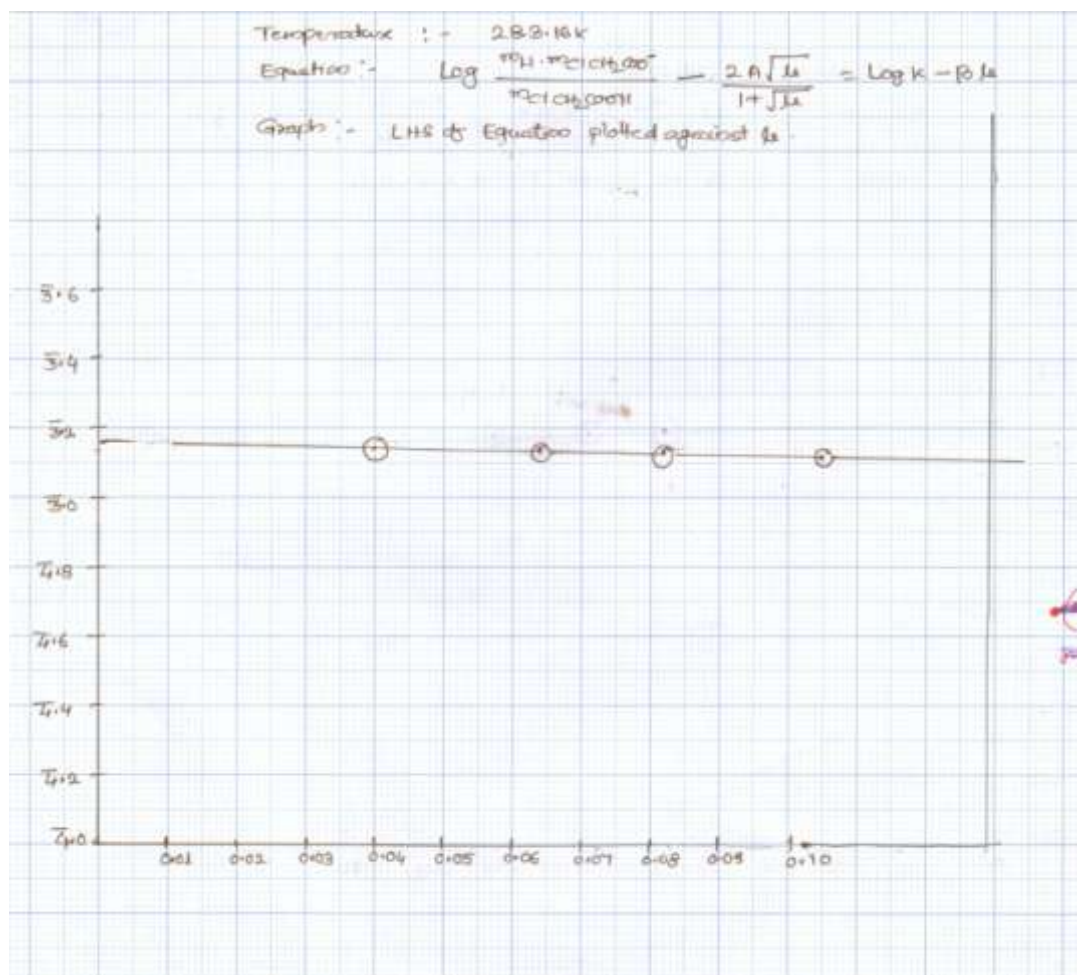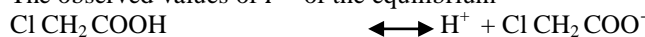

Fig:- I

Fig:-2

By the methods of least square values of depratonation constant are given by the equation

-log K = $\frac{A}{T}$ + B + CT + DT^2 --- (vii)

The observed values of P^K of the equilibrium

$$Cl\,CH_2\,COOH \xleftrightarrow{\hspace{2cm}} H^+ + Cl\,CH_2\,COO^-$$

has been found to fit well in the equation over the entire range of temperature studied. By simple method of elimination the value of constant were calculated as

A= 321.77, β = 1.4374, C= - 5.8586 X 10^{-3} and D = 2.3329 X 10^{-5}

Substituting the values of A,B,C,D in equation (viii) we get

P^K $\frac{321.77}{T}$+ 1.4374 – 5.8586 X 10^{-3} T + 2.3329 X 10^{-5} X T^2 ------------------------------------(viii)

The P^K values were calculated for the whole range of temperature studied and are given in Table II

TABLE II

Temp (0_K)	P^K (observed)	P^K Calculated Eq^0 (viii)	Difference
278.16	2.769	2.769	0.000
283.16	2.783	2.785	- 0.002
288.16	2.806	2.803	- 0.003
298.16	2.843	2.844	-0.001
308.16	2.889	2.891	- 0.002

The numerical values of thermodynamic quantities such as ΔG^0 and $\Delta H^0, \Delta S^0, \Delta Cp^0$ (Heat capacity change) accompanying the dissociation of one mole of $CH_2Cl\,COOH$ were calculated from equation (ix to xii) respectively.

$\Delta G^0 = -RT \ln K = 2.30259\ R\ (A + BT + CT^2 + DT^3)$ -------------------------------------- (ix)

$\Delta S^0 = \frac{-\partial(\Delta G^0)}{\partial T} = 2.30259\ R\ (-B - 2CT - 3DT^2)$ --(x)

$\Delta H^0 = \Delta G^0 + T\Delta S^0 = 2.30259\ R\ (A - CT^2 - 2DT^3)$ ------------------------------------ (xi)

$\Delta Cp^0 = \frac{\partial}{\partial T} (\Delta H^0) = 2.30259\ R\ (-2CT - 6DT^2)$ -------------------------------------(xii)

The values of ΔG^0, ΔH^0, ΔS^0 and ΔCp^0 were calculated and tabulated in the table III

TABLE III

Temp $0/$ K	$-\Delta H^0$ Cal	$+\Delta G^0$ Cal	$-\Delta S^0$ Cal	$-\Delta Cp^0$ Cal
278.16	1048.6	3524.7	16.44	34.64
283.16	1225.2	3608.5	17.07	36.17
288.16	1409.9	3695.5	17.72	37.73
298.16	1808.3	3879.3	19.06	40.95
308.16	2229.4	4076.8	20.46	44.30

Conclusion :- From the table III, the values of ΔH^0, ΔG^0, ΔS^0 and ΔCp^0 are 1803 ± 10 Cal. , 3879 ± 5.0 Cal., 19.06 ± 0.01 Cal and 40.95 ± 0.02 Cal. Respectively per mole st 298.16 K for the reaction $CH_2Cl\,COOH \longleftrightarrow H^+ + CH_2ClCOO^-$

Since,the values of the thermodynamic functions are all based on the dissociation constant and the dissociation constant calculated in this paper are most accurate, hence the values of ΔH^0, ΔG^0, ΔS^0 and ΔCp^0 may also be taken as most accurate values reported so far.

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