

## Standard Electrode Potential of Hg | Hg<sub>2</sub>Cl<sub>2</sub>(s), Cl<sup>-</sup> Electrode in Dioxane-Water Media at a Number of Temperature and the Related Thermodynamic Quantities

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### ABSTRACT

From e.m.f measurements of cells (C-1) and (C-2) it has been established that modified Davies equation is valid in dioxane-water media at least upto 30% dioxane by weight.  $E_m^0$  values of Hg | Hg<sub>2</sub>Cl<sub>2</sub>(s), Cl<sup>-</sup> electrode in dioxane-water media having 10, 20 and 30% dioxane by weight and the corresponding thermodynamic parameters have been determined at 288.15, 298.15, 308.15 and 318.15 °K.

(Pt),H<sub>2</sub> ( 1 atm ) | HCl(m<sub>1</sub>) x% Dioxane (100-x)% H<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>(s) | Hg ... (C-1)

(Pt),H<sub>2</sub> ( 1 atm ) | HCl(m<sub>1</sub>) BaCl<sub>2</sub>(m<sub>2</sub>)x% Dioxane (100-x)% H<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>(s) | Hg ... (C-2)

**Keywords :** Standard electrode potential, modified Davies equation, dioxane-water, mercuric-mercuric chloride electrode, thermodynamic quantities.

## I. INTRODUCTION

$E_m^0$  values of Hg | Hg<sub>2</sub>Cl<sub>2</sub>(s), Cl<sup>-</sup> electrode in dioxane-water have been reported by Schwabe and Schwenke<sup>1</sup> at one temperature only (298.15°K) that too after using Davies equation for activity coefficient. The use of this equation has been criticized by many workers<sup>2-6</sup>. We need the values of  $E_m^0$  of this electrode at different temperatures in connection with our projected study. Thermodynamics of this electrode in many mixed aquo-organic media also are not known, so the cells (C-1) and (C-2) were set up.

(Pt)<sub>1</sub>H<sub>2</sub> (1 atm) | HCl(m<sub>1</sub>) x% Dioxane (100-x)% H<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>(s) | Hg ... (C-1)

(Pt)<sub>1</sub>H<sub>2</sub> (1 atm)|HCl(m<sub>1</sub>) BaCl<sub>2</sub>(m<sub>2</sub>)x% Dioxane x% Dioxane (100-x)% H<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>(s)|Hg ... (C-2)

(where x = 10, 20, and 30) to find the  $E_m^0$  values Hg | Hg<sub>2</sub>Cl<sub>2</sub>(s), Cl<sup>-</sup> electrode in these media. Incidentally we wanted to confirm the validity of modified Davies equation for activity of ions in these media.

## RESULTS AND DISCUSSION

The e.m.f. of the cells (C-1) and (C-2) is given by

$$E = E^0 - k \log m_{H_2} \cdot m_{Cl} - k \log \gamma_{H_2} \cdot \gamma_{Cl} \quad \dots(1)$$

( $k = 2.3026RT / F$ )

which after substitution of equation (2)

$$\log \gamma_i = - ((AZ^2_i \sqrt{\mu}) / (1 + \sqrt{\mu})) + \beta_i \mu \quad \dots(2)$$

and rearrangement, gives

$$E + k \log m_{H_2} \cdot m_{Cl} - (kAZ^2_i \sqrt{\mu}) / (1 + \sqrt{\mu}) = E^0 - k \beta \mu \quad \dots(3)$$

putting the L.H.S. = y, the equation (3) becomes

$$y = E^0 - k \beta \mu \quad \dots(4)$$

HCl and BaCl<sub>2</sub> dissociate completely, so the value of ionic strength,  $\mu$ , in cells (C-1) and (C-2) are given by  $m_1$  and  $(m_1 + 3m_2)$ . All the quantities of L.H.S. of equation (3) being known ( $A$  and  $k$  from literature<sup>13</sup>)  $y$ 's were plotted against  $\mu$ 's at all temperatures for all the solvent system studied. All the plots were found to be linear, the intercept giving the values of  $E^0_m$  and slopes giving the value of  $\beta$ . The value of  $E^0_m$  against different mass % of dioxane at different temperatures are recorded in Table 1. The  $E^0_m$  values at different temperature fit in the equation (5) for the mixed solvent under study

$$E^0_m = a + b(t-25) + c(t - 25)^2 \quad \dots(5)$$

The values of 'a', 'b' and 'c' have been determined by the least square method and are recorded in Table 2. The recorded values of  $E^0_m$  from equation (5) agree with experimental values within 0.0003 for 10% and within 0.00001 for 20 and 30%. For >30% dioxane by weight, deviation occurs, so we did not proceed further with modified Davies equation.

The mean activity coefficient values ( $\gamma_{\pm}$ ) of hydrochloric acid in dioxane-water mixtures at 288.15, 298.15, 308.15 and 318.15 °K calculated using equation (2) agreed closely with the recorded values. Linearity of the plots shows the constancy of  $\beta$  values upto  $\mu$  ca 0.1 mol kg<sup>-1</sup>. The constancy of  $\beta$  values obtained with cells (C-1) and (C-2) and close agreement of the values  $\beta$  determined with those found earlier in this laboratory indicates the validity of equation (2) over the temperature and concentration range of the solvents studied.

The thermodynamic quantities  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for the overall reaction



in each of the dioxane-water media at each of the temperatures considered have been calculated by using well-known relationships from equation (5). These are recorded in Table 3.

It will be seen from the table that  $\Delta G^0$  values at all temperatures and concentrations of the organic component in the media are negative having almost constant values, the values are increasing slightly both with increase of temperature and increase of the concentration of the organic component in the media. It appears therefore that reaction (eq. 6) is spontaneous and is slightly more facilitated both by rise of temperature and rise in the concentration of the organic component in the media. The values of  $\Delta H^0$  in all cases are negative indicating the process to be exothermic and the products formed to be more stable the stability and exothermicity increasing steadily with rise in temperature.  $\Delta H^0$  seem to decrease with increase in concentration of the organic component from 10 to 20%, but thereafter  $\Delta H^0$  values seem to attain almost constant values indicating perhaps that the above reaction is completed in ca 20% of the organic component of the media. This idea gains additional support from a perusal of the  $\Delta S^0$  values.  $\Delta S^0$  values are negative throughout indicating the system remains more ordered; the negativity and hence orderliness increasing steadily with rise in temperature. However again  $\Delta S^0$  values at 20° and 30% of dioxane content in the media are almost the same at all temperatures.

These thermodynamic data can be systemized and explained as follows in the light of Frank and Wen's ideas<sup>14</sup>. Water may be supposed to be an equilibrium mixture of monomeric H<sub>2</sub>O molecules and three dimensional network of H-bonded tetra coordinated H<sub>2</sub>O molecules.



As the reaction (6) proceeds to the R.H.S., H<sup>+</sup> and Cl<sup>-</sup> are solvated more and more by these monomeric H<sub>2</sub>O molecules liberating heat the region A of Frank and Wen gets enhanced decreasing region B, the system gets ordered. When dioxane is added to the media, dioxane being aprotic it will combine with the proton part of H<sub>2</sub>O(m), causing further orderliness and exothermicity of heat. It appears that both these processes get saturated at ca 20% of dioxane component of the media.

## EXPERIMENTAL

All the chemicals were of AR/GR grade, still their purity were analytically determined by standard methods<sup>7</sup>. Stock solution of hydrochloric acid and HCl + BaCl<sub>2</sub> in approximately equimolar proportion was prepared. Experimental solutions were prepared by appropriate dilution of the stock solution. The stoichiometric molalities were correct to micromol kg<sup>-1</sup>. Dioxane was purified following the method of Das and coworkers<sup>8</sup>. The Hg | Hg<sub>2</sub>Cl<sub>2</sub> (s), Cl<sup>-</sup> electrode was prepared and set up as recommended by Hills and Ives except applying the silicone treatment as reported from this laboratory earlier<sup>9-10</sup>.

All the cells were set up in duplicate. The e.m.f. reading of the duplicate cells attained constant value after 3 to 4 hours of their introduction in the thermostat and slowly bubbling H<sub>2</sub> gas and these e.m.f. values remained constant at least over 1½ hours thereafter. The e.m.f. of the duplicate cells agreed generally within 0.02 mV, the mean of which after necessary correction for barometric pressure, vapour pressure band bubbler depth<sup>11</sup>

were recorded. The vapour pressure of the mixed solvent at each temperature was calculated by using Akerl of equation<sup>12</sup>. The e.m.f. correction,  $\Delta E$  was added to observe e.m.f. values to get the corrected e.m.f. values.

**TABLE - 1**

The value of standard Electrode Potential ( $E_m^0$ ) of Hg | Hg<sub>2</sub>Cl<sub>2</sub>(s), Cl<sup>-</sup> Electrode in Molal Scale in abs. Volt.

Temp. °K	10% (m/m) D-W	20% (m/m) D-W	30% (m/m) D-W
288.15	0.25960	0.25715	0.25270
298.15	0.25583	0.25012	0.24467
308.15	0.25018	0.24248	0.23530
313.15	0.24233	0.23684	0.22567

m/m = mass/mass

D-W = Dioxane-water

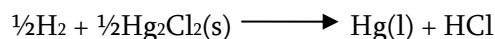
**TABLE - 2**

Value of a, b, c calculated by equation  $E_m^0 = E_{0.25}^0 + b(t-25) + c(t-25)^2$

Mass % Dioxane	a/V	-b x 10 <sup>4</sup> VK <sup>-1</sup>	-C x 10 <sup>6</sup> V K <sup>-2</sup>
10	0.25583	2.12	7.07
20	0.25012	7.595	3.75
30	0.24467	7.595	3.75

**TABLE - 3**

Thermodynamic Functions for the Reaction:



Temp. °K	10% (w/w) D-W			20% (m/m) D-W			30% (m/m) D-W		
	$-\Delta G^0$ (kJ/mol)	$-\Delta S^0 \times 10^3$ (kJK <sup>-1</sup> mol <sup>-1</sup> )	$-\Delta H^0$ (kJ/mol)	$-\Delta G^0$ (kJ/mol)	$-\Delta S^0 \times 10^3$ (kJK <sup>-1</sup> mol <sup>-1</sup> )	$-\Delta H^0$ (kJ/mol)	$-\Delta G^0$ (kJ/mol)	$-\Delta S^0 \times 10^3$ (kJK <sup>-1</sup> mol <sup>-1</sup> )	$-\Delta H^0$ (kJ/mol)
288.15	25.048 ±0.004	6.95 ±0.11	27.04 ±0.04	24.619 ±0.004	66.04 ±0.11	43.65 ±0.04	24.382 ±0.004	66.04 ±0.11	43.41 ±0.04

298.15	24.877 ±0.004	20.45 ±0.12	30.97 ±0.04	24.133 ±0.004	73.28 ±0.12	45.98 ±0.04	23.607 ±0.004	73.28 ±0.12	45.45 ±0.04
308.15	24.218 ±0.004	33.961 ±0.13	34.68 ±0.04	23.316 ±0.004	80.51 ±0.13	48.20 ±0.04	22.703 ±0.004	80.51 ±0.13	47.51 ±0.04
318.15	23.382 ±0.000 4	47.47 ±0.13	38.48 ±0.04	22.852 ±0.004	87.75 ±0.13	50.77 ±0.04	21.774 ±0.004	87.75 ±0.13	49.61 ±0.04

$\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are in  $\text{kJmol}^{-1}$ ,  $\text{kJmol}^{-1}$  and  $\text{kJK}^{-1}\text{mol}^{-1}$ , respectively.

D-W = Dioxane-water

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