STANDARD POTENTIALS OF CALOMEL ELECTRODE IN WATER + ACETIC ACID MIXTURES AT 25°C

P.K. Samanta and U.N. Dash*

Research & Control Laboratory (Chemical Section), Rourkela Steel Plant, SAIL, Rourkela-769011
** P.G. Department of Chemistry, Utkal University, Bhubaneswar-751004.*

The electromotive force measurements of cells of the type,

$$Ag(s)/AgCl(s)/KCl(c)//KCl(c)/Hg_2Cl_2\ (c)/Hg(l)$$

are used to determine the standard potentials of the calomel electrode in 10,20,40 & 60 wt% acetic acid + water mixtures at 25°C. The standard thermodynamic quantities associated with the electrode reactions have been evaluated and compared with that available in other mixed solvents.

Very recently, Dash et al [1] reported the standard potentials of calomel electrode in different compositions of water + urea, + d-glucose and + d-fructose mixtures at different temperatures and discussed the results on the prefential solvation of chloride ion in these solvents. The present work aims at evaluating the standard potential of this electrode in acidic medium.

EXPERIMENTAL

Glacial acetic acid and calomel (BDH AnalaR) were used without further purification. Potassium chloride (AnalaR) was dried at 100°C for 2 hr and kept in a vacuum desiccator over anhydrous calcium chloride until required.

Solvents of various compositions were made up by weight using glacial acetic acid (BDH) and conductivity water. 0.1 molar potassium chloride stock solutions were prepared in the respective water + acetic acid mixed solvents. The cell solutions of the required molarities were then prepared from the stock solutions by double dilution method using the corresponding mixed solvent. The silver-silver chloride and calomel electrodes were prepared as described earlier [1,2] and the cell

$$Ag(s)/AgCl(s)/KCl(c)//KCl(c)/Hg_2Cl_2(s)/Hg(l)$$

was set up as described in ref 1 using potassium chloride solutions in acetic acid-water mixtures (10,20,40 and 60% acid). Potential measurements were carried out at 25 ± 0.05° C as described earlier [1].

RESULTS AND DISCUSSION

The results of the emf measurements for the cell (A) are presented in Table-1. The emf of cell (A) is given by the expression [1],

$$E = E^\circ_{cal} - E^\circ_{Ag,AgCl} \qquad ....(1)$$

$E^\circ_{Ag,AgCl}$ is the standard molar potential of the silver/silver chloride electrode and obtained from the E°_m values [3] using the density values of various solvents at 25°C. The values of E°_c of the silver/silver chloride electrode in 10,20,40 and 60 wt% acetic acid mixture are 0.21105 ; 0.1980 ; 0.1643 and 0.1144 V, respectively at 25°C. E°_{cal} the standard molar potential of the calomel electrode is calculated for solution of each concentration (Table-1). The E°_c values of the calomel electrode are seen to remain almost constant with change of molarity. The average of these E°_c values was considered to be the true E°_c value of the calomel electrode. These values are also recorded in the table along with the standard deviation at the end of the column. As usual[4], the standard electrode potentials on the molal (E°_m) and mole fraction (E°_N) scales have been computed from the values of E°_c, and are shown in Table 2 along with those in water [1].

The standard Gibbs free energy change, ΔG°_m on the molal scale for the electrode reaction,

$$\tfrac{1}{2} Hg_2Cl_2\ (s) + e \rightleftharpoons Hg(l) + Cl^-\ (solvated)$$

in various solvents has been evaluated at 25°C from E°_{cal} on molal scale and is listed in Table-2.

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TABLE 1

Emf DATA OF CELL (A) IN VARIOUS WATER + ACETIC ACID MIXTURES AT 25° C.

10^2 C	wt% acetic acid							
	10		20		40		60	
mol dm^{-3}	E	E'_o	E	E'_o	E	E'_o	E	E'_o
0.5	0.0485	0.2595	0.0442	0.2422	0.0489	0.2132	0.0504	0.1648
1.0	0.0480	0.2590	0.0443	0.2423	0.0490	0.2133	0.0508	0.1652
2.0	0.0483	0.2593	0.0441	0.2421	0.0490	0.2133	0.0502	0.1646
4.0	0.0483	0.2593	0.0440	0.2420	0.0493	0.2136	0.0505	0.1649
5.0	0.0479	0.2589	0.0442	0.2422	0.0495	0.2138	0.0505	0.1649
6.0	0.0479	0.2589	0.0444	0.2424	0.0492	0.2135	0.0506	0.1650
8.0	0.0483	0.2593	0.0442	0.2422	0.0493	0.2136	0.0502	0.1646
10.0	0.0482	0.2592	0.0441	0.2421	0.0492	0.2135	0.0507	0.1651
Average ;		0.2591		0.2420		0.2134		0.1648
Value ;		± 0.0001		± 0.0002		± 0.0001		± 0.0001

For the transfer, process,

Cl^- (water) $\longrightarrow$ Cl^- (in water + acetic acid), the Gibbs free energy change, ΔG_t° of transfer has been calculated on the mole-fraction scale [4], since that eliminates the free energy change due to the concentration change and is presented in Table-2.

An inspection of Table-2 shows that E° values for the calomel electrode decrease with the increasing acetic acid content of the solvent system. The observed decrease is in agreement with the electrostatic charging (Born) effect of the media. A comparison of the E° values of the electrode in water + urea, +d-glucose, +d-fructose and +acetic acid mixtures at 25° C shows that the E° values decrease in the order: water + urea $\succ$ water + d-glucose/water + d-fructose $\succ$ water + acetic acid, which is the order of their dielectric constants.

The change in ΔG_m° value on passing from water to various solvents (Table-2) is due to variation of free energy of solvation. The observed increase in ΔG_m° (i.e. becoming less negative) with increasing proportion of acetic acid in water points to the fact that as the dielectric constant of the medium decreases with increasing acetic acid content, more work is required to keep the ions apart and therefore, less work is produced by the electrode reaction and less negative free energy changes result. It may be concluded that Cl^- ion is less solvated in mixed solvents and solvation decreased with increasing acid contents of the solvent system.

TABLE 2

VALUES OF THE STANDARD POTENTIALS OF THE CALOMEL ELECTRODE ON THE MOLAR, MOLAL & MOLE-FRACTION SCALES AND STANDARD MOLAL FREE-ENERGY CHANGE, TRANSFER GIBBS FREE ENERGY CHANGE AND PRIMARY MEDIUM EFFECT (MOLE-FRACTION SCALES) OF Cl^- ION IN VARIOUS WATER + ACETIC ACID MIXTURES AT 25° C.

Wt% acetic acid	E_c°	E_m°	E_N°	$-\Delta G_m^\circ$ KJ/ mol	ΔG_t° KJ/ mol	Pry. med. effy
	volts					
0	0.3336	0.3338	0.1274	32.21	-	-
10	0.2591	0.2585	0.0559	24.94	6.90	1.21
20	0.2420	0.2408	0.0422	23.24	8.22	1.44
40	0.2134	0.2111	0.0216	20.37	10.21	1.79
60	0.1648	0.1619	-0.0165	15.62	13.88	2.43

It is of interest to compare the Gibbs free energy change for the electrode reactions,

$$\tfrac{1}{2}Hg_2Cl_2(s) + e \rightleftharpoons Hg(l) + Cl^- \text{ (solvated)}$$

and $$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^- \text{ (solvated)}$$

in mixed solvents at 25°C. The free energy changes due to solvation of Cl^- in the latter electrode reaction (-20.31, -18.99, -15.64 and -10.76 KJ) are lower than that in the former reaction (-24.94, -23.24, -20.37 and -15.62 KJ) in 10,20,40 and 60 wt% acetic acid, respectively. This suggests that Cl^- ion is less solvated in presence of Ag^+ ion than in presence of Hg_2^{2+} ion in these media. It is

thus clear that the anionic solvation depends on the associated cation. Smaller size of the Ag^+ ion (as compared to the Hg_2^{2+} ion) leads to the greater ion-ion interaction resulting in the lower free energy of solvation of Cl^-

A perusal of Table 2 shows that as the proportion of acetic acid increases, the ΔG_t° value for the Cl^- ion becomes increasingly positive. The positive ΔG_t° values signify that the transfer of Cl^- ion from water to water + acetic acid mixtures is not favourable. The primary medium effect of various water + acetic acid mixtures upon Cl^- ion have been computed in the mole - fraction scale at 25° C as mentioned earlier [1] and these are recorded in Table-2. It is seen that the medium has a greater effect upon the Cl^- ion as the acetic acid content is gradually increased. The increasingly positive values of this quantity suggest that the escaping tendency of the Cl^- ion is greater in water + acetic acid media than in pure water. This is in support of the view that the Cl^- ion is less stabilized in the mixed solvents than in water medium.

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