STANDARD POENTIALS OF CALOMEL ELECTRODE IN WATER + UREA, + D GLUCOSE AND D FRUCTOSE MIXTURES AT DIFFERENT TEMPERATURES

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The standard potentials of the calomel electrode in water mixed with different percentages of urea, D glucose and D fructose have been determined at different temperatures from the electromotive force measurements of cells of the type.

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

The results have been discussed in terms of preferential solvation of ions.

Although the calomel electrode has long been used as a reference electrode in aqueous and non-aqueous media, its potentials were known only in water and formamide over a range of temperatures. So far no attempt has been made for determination of its potentials in mixed solvents. The present work has been undertaken as a part of our programme on potential studies in mixed solvents <3>. Standard potentials of the calomel electrode in water + urea mixtures containing 11.52, 20.31, 29.64 and 36.83 wt % urea at seven different temperatures ranging from 5° to 35°C, in water + D glucose mixtures containing 5, 10, 20 and 30 wt % D glucose and water + D fructose mixtures containing 5 and 10 wt % D fructose, at 25° have been determined and reported here.

EMF of the cells

$$Ag(s) \mid AgCl(s) \mid KCl(c) \parallel KCl(c) \mid Hg_2Cl_2(s) \mid Hg(l) \quad \ldots\ldots\ (A)$$

have been measured in different mixed media to determine the standard potentials of the calomel electrode at different temperatures.

EXPERIMENTAL

Potassium chloride (E.Merck, G.R), calomel (B.D.H., AnalaR), urea (B.D.H., AnalaR), D glucose (Merck) and D fructose (B.D.H., AnalaR), were used without further purification.

Solvent media of various compositions were made up by weight in conductivity water. Stock solutions of potassium chloride were prepared on the molar scale in the respective mixed solvents. The stock solvents, as well as potassium chloride solutions, were kept at low temperature (5°C). The solutions of the required molarities were then prepared by further dilution of the stock solution using the corresponding mixed solvent.

The silver/silver chloride electrodes were prepared by standard methods <4>. Metallic mercury was purified in accordance with the procedures suggested by Hills and Ives<4>, and Hullet <5>. Triple-distilled and vacuum dried mercury, and calomel were used for preparation of the calomel electrode.

The cell vessles for cell (A) are of the type recommended by Hills and Ives <4> The emf measurements were made using a Bajaj (India) potentiometer in conjuction with a d.c. galvanometer (OSAW) and a Weston standard cell (Muirhead and Co., England). All measurements were made in a water thermostat maintained at specified temperature ± 0.05°C.

The cells were carefully washed and dried. About 2 ml of pure triply distilled mercury was added to the cell compartment which served as the calomel half cell. An intimate mixture of mercury - mercurous chloride was prepared by rubbing about 0.5 g of calomel (solid) with one or two globules of mercury on an agate mortar in the dry state. A little of this paste was then poured into the cell compartment so that it formed a very thin layer on the surface of the mercury. Sufficient potassium chloride solution of the known molarity in the respective mixed solvent to cover the mercury - mercurous chloride

was transferred to the cell compartment. Potassium chloride solution of the same molarity in the corresponding mixed solvent was transferred to the other cell compartment and the silver/silver chloride electrode which showed a potential difference of 0.1 mV or less on being mutually compared with each other, after being rinsed in potassium chloride solution, was then placed in position. The cells were transferred to a water thermostat and the emf measurement was taken 45 min after setting up of the cells. Constancy of the emf readings to ± 0.2 mV for 1 1/2 h was considered the criterion of equilibrium.

RESULTS AND DISCUSSION

As usual, the emf, E of cell (A) is given by the expression,

$$E^\circ = E^\circ_{cal} - E^\circ_{Ag/AgCl} \quad \ldots\ldots\ldots \quad (1)$$

or E°_{cal} should be equal to $E + E^\circ_{Ag/AgCl}$ and is expected to be independent of concentration and equal to the standard potential of the calomel electrode in the particular medium. In the present case, it was found to be slightly dependent on concentration (a change of 0.2 to 0.4 mV per change in 0.1 molar unit in conecentration).

The standard potential function E°_{cal} $(E+E^\circ_{Ag/AgCl})$ at different concentrations of KCl is calculated making use of observed emf of the cell E and $E^\circ_{Ag/AgCl}$ value in the corresponding medium and temperature <6-8>. This is plotted as a function of c and extrapolated to c = 0 to get the standard potential of the calomel electrode E°_C in the specified medium and temperature. These are given in Table 1. The average standard deviation in the values of E°_{cal} is ± 0.3 mV. The standard electrode potentials on the molal (E°_m) and mole-fraction (E°_N) scales have been computed from E°_c by the usual equation <3>.

The E°_{cal} values at various temperatures for any medium are fitted by the method of least squares to the equation

$$E^\circ = a + b\,(t - 25) + c\,(t - 25)^2 \quad \ldots.(2)$$

where t is any temperature (° c). The constant a, b, and c of equation (2) on different scales are shown in Table-2. The average deviation between the experimental values and the values calculated from equation (2) is within ± 0.3 mV.

The standard thermodynamic quantities (ΔG°_m, ΔH°_m and ΔS°_m) on the molal scale for the electrode reaction,

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

in various solvents have been evaluated at 25° C by the usual relations <3> and are presented in Table-3. The standard transfer thermodynamic quantities (ΔG°_t ΔH°_t and ΔS°_t) for the process, Cl^-(water)---> Cl^- (in mixed solvent) have been evaluated for various solvents. These quantities on the mole-fraction basis <4> are presented in Table-3 along with the E° values for various solvents.

The E° values in different solvents vary because of the difference in solvation of Cl^- ion in these solvents. Any change in E° value on passing from water to a given medium is due to variation of solvation. As observed, the E° value increases with the increase in urea content in water + urea mixtures whereas it decreases in water + sugar mixtures with the increase in sugar content. The observed increase in the E° values with the increase in dielectric constant of the water + urea mixtures

TABLE 1

STANDARD MOLAR POTENTIALS (E°_C IN ABS. V) FOR THE CALOMEL ELECTRODE IN WATER + UREA MIXTURES AT DIFFERENT TEMPERATURES

Wt% urea	Temperature t° C						
	5	10	15	20	25	30	35
11.52	0.3156	0.3146	0.3132	0.3119	0.3100	0.3083	0.3069
20.31	0.3367	0.3350	0.3321	0.3296	0.3280	0.3263	0.3250
29.64	0.3483	0.3462	0.3445	0.3426	0.3409	0.3395	0.3378
36.83	0.3589	0.3570	0.3554	0.3535	0.3518	0.3503	0.3480

TABLE 2

EFFECT OF TEMPERATURE ON STANDARD POTENTIAL CONSTANTS OF EQN. (2) FOR MOLAR (C), MOLAL (M) MOLE-FRACTION (N) SCALES IN WATER + UREA MIXTURES

	a	-b x 10^4	c x 10^6
	Urea 11.52%		
c	0.3100	3.47	-2.24
m	0.3086	3.13	-0.88
N	0.1065	9.92	-0.96
	Urea 20.31%		
c	0.3280	3.24	5.65
m	0.3254	3.39	4.90
N	0.1269	10.03	5.33
	Urea 29.64%		
c	0.3509	3.24	2.02
m	0.3370	3.16	2.30
N	0.1426	9.64	2.76
	Urea 36.83%		
c	0.3518	3.45	0.13
m	0.3469	3.43	0.83
N	0.1561	9.76	0.41

the proportion of urea increase), is in agreement with the electrostatic charging (Born) effect of the media. The variation of E° values in water sugar mixtures lends support to the linear correlation between the E° and reciprocal of the dielectric constant of the solvent concerned.

Any change in ΔG°_m on passing from water to various solvents is due to variation of free energy of solvation. The higher free energy due to solvation of Cl^- ion in 29.64 and 36.83 wt% urea may be due to the fact that Cl^- is more solvated in these solvents than in water and the solvation increases as the proportion of urea increases. The lower free energy in water sugar mixed solvents as well as in 11.52 and 20.31 wt% urea suggests that Cl^- ion is less solvated in these solvents and solvation decreases with increasing D-glucose or D fructose content of the solvent system. The standard enthalpy and entropy changes for water + urea systems are all negative, but the solvent effect on the magnitude of these quantities appears to be irregular. The difference in magnitude of the ΔH°_m and ΔS°_m values may be due to some structural effects. These effects can arise from solvation properties alone or in combination with the solvent properties in the different solvent mixtures. However, the solvent effect on the standard potentials of the electrode can be examined from the related quantities of Gibbs free energy of transfer of Cl^- ion from water to the solvent concerned, since the Gibbs free energy of transfer is an important index of the differences in interactions of the ion and the solvent molecules in the two different media.

As can be seen from Tabel 3, the values of ΔG°_t for the transfer of Cl^- ion from water to water + D glucose and water +D fructose mixtures appear to be positive and become increasingly positive as the proportion of the sugars increases, whereas the ΔG°_t value decreases with increase of the urea content in the mixture and becomes negative in 29.64 and 36.83 wt% urea. The positive values of ΔG°_t signify that the transfer of Cl^- ion from water to water + D glucose, water + D fructose and water + urea (except urea - rich mixtures) mixture is not favourable. Thus, the Cl^- ion appears to be in a lower Gibbs energy state & hence, more strongly stabilized in water than in these mixed solvents. The negative ΔG°_t value indicates that the transfer of Cl^- ion from water to urea-rich mixed solvents is favourable, and the ion appears to be in a lower Gibbs energy state in 29.64 and 38.83 wt% water urea mixtures. It is known that all structure - forming processes, including solvation of ions, are exothermic and accompained by a decrease in entropy, and the structure breaking processes, including desolvation of ions, are endothermic and accompained by entropy gain. The negative values of ΔH°_t and ΔS°_t for the transfer of Cl^- from water to water + urea mixtures substantiate this view.

The primary medium effect which results from a difference of the ion-solvent interactions at infinite dilution in each solvent can be represented by

$$\lim_{N \to 0}(\log {}^s\gamma_\pm) = 2\,(-E^\circ_N - -E^\circ_N)/2.3026(RT/F) \quad (3)$$

where the limit term indicates the primary medium effect. As the magnitude of this effect indicates the stabilization of the ion in the solvent concerned, the positive magnitude of this quantity in water-rich-urea mixtures and negative magnitude in urea-rich mixtures suggest that the escaping tendency of the Cl ion is more in water-rich mixed solvents but less in

TABLE 3

VALUES OF THE STANDARD POTENTIALS ON THE MOLAR, MOLAL, AND MOLE-FRACTION SCALES, STANDARD THERMODYNAMIC QUANTITIES* (ON THE MOLAL SCALE), TRANSFER THERMODYNAMIC QUANTITIES* (ON THE MOLE-FRACTION SCALE) AND PRIMARY MEDIUM EFFECT AT 25°C.

Wt% additive	E°_c (V)	E°_m (V)	E°_N (V)	$-\Delta G^\circ_m$ /	$-\Delta H^\circ_m$ /	$-\Delta S^\circ_m/\Delta G^\circ_t$ /		ΔH°_t /	ΔS°_t /		$\lim(\log\gamma_\pm)$ N-->0
				a	a	b	a	a	b		
0	0.3336	0.3338	0.1274	64.4	-	-	-	-	-		-
	Urea										
11.52	0.3100	0.3086	0.1065	59.6	78.8	64.6	2.02	24.5	88.9		0.7066
20.31	0.3280	0.3254	0.1269	62.8	87.7	83.6	0.05	26.8	90.0		0.0170
29.64	0.3409	0.3370	0.1426	65.0	83.5	62.4	-1.47	27.2	86.2		-0.5138
36.83	0.3518	0.3469	0.1561	66.9	86.4	65.2	-2.77	28.8	87.4		-0.9702
	D glucose										
5	0.2723	0.2721	0.0680	52.5	-	-	5.73	-	-		2.003
10	0.2642	0.2638	0.0622	50.9	-	-	6.29	-	-		2.204
20	0.2551	0.2543	0.0581	49.1	-	-	6.69	-	-		2.243
30	0.2471	0.2458	0.0556	47.4	-	-	6.93	-	-		2.427
	D fructose										
5	0.2652	0.2650	0.0609	51.1	-	-	6.42	-	-		2.248
10	0.2608	0.2604	0.0588	50.3	-	-	6.62	-	-		2.319

(a) Free energy and enthalpy Units are KJ/mole (b) Entropy units are Joules/mole/deg
* Uncertainties $\Delta G^\circ = \pm 6$J, $\Delta H^\circ = \pm 6$ J, in $\Delta S^\circ = \pm 3$ J, $\Delta G^\circ_t = \pm 5$ J, $\Delta H^\circ_t = \pm 6$ J, and $\Delta S^\circ_t = \pm 2$ J.

urea-rich mixed solvents than in pure water. This is consistent with the conclusions based on the fact that the Cl^- ion is more strongly stabilized in urea-rich mixed solvents than in aqueous medium. The positive values of the primary medium effect in water + D glucose and water + D fructose solvent systems suggest that the escaping tendency of the Cl^- ion is greater in these solvents than in water, and therefore, the ion is less solvated in these mixed solvents than in aqueous medium.

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