STANDARD POTENTIALS OF MERCURY – MERCUROUS SULPHATE ELECTRODE AND TRANSFER THERMODYNAMIC QUANTITIES IN DIFFERENT BINARY SOLVENT SYSTEMS

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Standard potentials of the mercury - mercurous sulphate electrode in different compositions of water with acetone, or ethylene glycol, or urea mixtures have been determined at four different temperatures from 5 C to 35 C from the electromotive force measurements of cells of the type.

$Ag|\ AgCl|\ KCl\ (c)\ ||K_2SO_4\ (C/2)|\ Hg_2SO_4\ |\ Hg$ (A).

These values have been used to evaluate the transfer thermodynamic quantities accompanying the transfer of 1 gram ion of the So_4^{2-} ion from the standard state in water to the standard state in the respective aqueo - organic solvent mixtures.

Neither in aqueous nor in mixed media does any work seem to have been doen on the determination of standard electrode potentials of mercury - Mercurous sulphate electrode over a range of temperatures. However, Jena and Prasad <1> used this electrode as a reference electrode for the determination of standard electrode potential of the silver - silver chromate electrode in water at 35°C. The standard potential of the mercury - mercurous sulphate electrode is also known in water <2> at 25°C. In continuation of the study on ion-solvent interactions in binary solvent systems <3>, we now report the standard potential of the mercury - mercurous sulphate electrode in water and various compositions of aqueous acetone, ethylene glycol, and urea mixtures at different temperatures ranging from 5°C to 35°C from the study of the cell.

$Ag,/\ AgCl/,KCl\ (c)//K_2SO_4\ (c/2)/,\ Hg_2SO_4/Hg,(A)$

EXPERIMENTAL

Potassium chroride (E. Merck, G.R.), potassium sulphate (BDH, AnalaR) and urea (BDH, AnalaR) were used without further purification. Acetone (BDH, AnalaR) was distilled with considerable rejection of head and tail fractions. This was repeated thrice. Ethylene glycol (E. Merck, G.R.) was mixed with magnesium oxide, kept overnight and vacuum distilled These solvents were stored in dark containers in a desiccator.

Silver - silver chloride electrode, mercury - mercurous sulphate electode and preparation of different salt solutions and solvent mixtures are all as described earlier <3,4>. Details of the cell and potential measurements are given in the preceeding paper <3>.

About 2mL pure mercury was placed in the cell compartment which served the mercury - mercurous sulphate half cell. An intimate mixture of mercury - mercurous sulphate was prepared by rubbing about 0.5 g of mercurous sulphate (solid) with one or two globules of mercury on an agate mortar in the dry state. A litle 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 sulphate solution in the respective mixed solvents to cover the mercury - mercurous sulphate was transferred to the cell compartment. Potassium chloride solution in the corresponding mixed solvent was transferred to the other cell compartment and the silver - silver chloride electrode half cell was prepared as described in the preceeding paper <3>. The cells were transferred to a water thermostat and the emf measurement was taken 45 min after setting up the cells. Constancy of the emf readings to ±0.2 mV for 1 1/2 hrs was considered the criterion of equilibruim. Conductances for the sulphate and chloride solutions in the range of concentrations used in the cell measurements needed for the calculation of the liquid junction potentials were

TABLE 1

STANDARD POTENTIALS OF THE MERCURY MERCUROUS SULPHATE ELECTRODE IN MOLAR SCALE AT DIFFERENT CONDITIONS.

Wt% organic compound	E° volts at temperature °C			
	5	15	25	35
0	0.6284	0.6223	0.6158	0.6091
Urea				
11.52	0.6405	0.6306	0.6207	0.6105
20.31	0.6557	0.6457	0.6348	0.6253
29.64	0.6651	0.6539	0.6430	0.6322
36.83	0.6729	0.6624	0.6524	0.6421
Ethylene Glycol				
10	0.6256	0.6121	0.5982	0.5852
30	0.6126	0.5997	0.5869	0.5732
Acetone				
10	0.6201	0.6078	0.5954	0.5829
20	0.6019	0.5904	0.5788	0.5673
30	0.5816	0.5728	0.5641	0.5556

TABLE 2

CONSTANT OF EQUATION (3)

Wt% of organic compound	a = E°_m(V)	-bx10³	cx10⁶
0	0.6161	0.6367	-1.0
Urea			
11.52	0.6192	0.9942	-0.75
20.31	0.6327	0.935	2.5
29.64	0.6391	1.0717	1.5
36.83	0.6474	1.0142	0.25
Ethylene Glycol			
10	0.5979	1.3242	1.25
30	0.5866	1.333	-2.0
Acetone			
10	0.5963	1.222	-0.5
20	0.5803	1.1093	0.25
30	0.5665	0.8233	0.10

measured by a digital direct reading conductivity meter (Systronics, Type 304) <6> at each temperature.

RESULTS AND DISCUSSION

As usual <3> the emf, E of the cell (A) is given by the expression

$$E = E^\circ_{Hg-Hg_2SO_4} + \frac{RT}{2F} \ln(2c) + \frac{RT}{2F} \ln \frac{\gamma_{Cl^-}}{\gamma_{SO_4}} + E_j \quad (1)$$

where the symbols have their usual significance.

The standard molar potential, E°_c of the mercury - mercurous sulphate electrode was obtained by the method of extraplating the auxiliary function E°_c to c=0 where E°_c is given by

$$E^\circ_m = E - 1/2\ K \log(2c) - \frac{1}{2}k\left\{\frac{4A\sqrt{3C/2}}{1+\sqrt{3C/2}} - \frac{2A\sqrt{C}}{1+\sqrt{C}}\right\} + E^\circ_{Ag,AgCl} - E_j = E^\circ_{Hg-Hg_2SO_4} + b\,c \quad (2)$$

to the molarity czo as described in the preceeding paper <3> $E^\circ_{Ag,AgCl}$ is the standard potential (on the molar scale) of the silver - silver chloride electrode, and A is the Debye-Huckel constant, and are known over the temperature range under investigation for water<7> and for various compositions of water + acetone<8>, Water + ethylene glycol <9> and water + urea<10> mixtures. The values of the liquid junction potentials, E°_j ; were calculated from the equivalent conductances of potassium sulphate and potassium chloride by means of Lewis and Sargent equation. It is found that the value of E°_j varied in the range 0.001 - 0.008 V in all solvents.

The E°_m values are recorded in Table 1. The standard electrode potentials on the molal (E°_m) and mole-fraction (E°_N) scales have been computed from (E°_m) by the usual equations <3>. The E° values at various temperatures for a given medium were fitted by the method of least squares, to the equation.

$$E^\circ = a + b(t-25)^2 + c\,(t-25)^3 \quad (3)$$

where t is any temperature (°C). The constants a, b and c of equation (3) on the molal scale are shown in Table 2. The average deviation between the experimental values and those values calculated from eqn (3) is within ±0.3 mV.

The standard thermodynamic quantities

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES IN WATER, WATER + UREA, ETHYLENE GLYCOL AND + ACETONE MIXTURES AT 25°C.

Wt % organic compound	ΔG_m° (kJ mol^{-1})	$-\Delta H_m^\circ$ (kJ mol^{-1})	$-\Delta S_m^\circ$ (J mol^{-1})	ΔG_t° (kJ mol^{-1})	$-\Delta H_t^\circ$ (kJ mol^{-1})	$-\Delta S_t^\circ$ (J mol^{-1})	lim $(\log^3\sqrt{\gamma_w})$ N --> 0
0	118.9	155.51	122.87				
Urea							
11.52	119.49	176.67	191.86	-1.43	20.2	62.97	-0.2502
20.31	122.10	175.87	180.44	-4.71	22.57	59.93	-0.8249
29.64	123.34	184.97	206.82	-6.75	28.93	74.39	-1.183
36.83	124.94	183.26	195.72	-9.01	26.97	60.25	-1.579
Ethylene Glycol							
10	115.38	191.54	255.55	2.78	35.31	127.8	0.4868
30	113.20	189.86	257.25	3.34	33.53	123.7	0.5849
Acetone							
10	115.08	185.24	235.83	3.11	29.1	108.07	0.5443
20	111.99	175.78	214.08	5.4	19.26	83.25	0.9466
30	109.32	156.67	158.89	7.3	1.14	28.24	1.275

(ΔG_m° ΔH_m° and ΔS_m°) for the electrode reaction,

Hg_2SO_4 (s) +2e --> 2Hg(l)+SO_4^{2-} (solvated)

in various solvents have been evaluated at 25°C and are presented in Table 3.

The E_m° values obtained in water at 25°C (0.6161 V) is in good agreement with the literature value (0.6158 V) at the same temperature <2>. An inspection of Table 1 shows that the standard electrode potentials of the mercury - mercurous sulphate electrode obtained in water are less than that in water + urea mixtures but more than that in water + acetone and water + ethylene glycol mixtures, the relative order being

Water + urea > water + ethylen glycol > water + acetone which reflects the electrostatic (coulomb) effects favoured by the decreasing dielectric constant of the medium. In water urea mixtures medium, a linear correlation between the E° and reciprocal of dielectric constant of the solvent holds good. The observed increase in the E° values of the electrode with the increase in dielectric constant of the water + urea mixtures (as the proportion of urea increases) is in agreeement with the electrostatic charging (Born) effect of the media. The higher values of E° in various compositions of water + urea mixtures than in water may also be explained by the higher basicity of water + urea mixtures which decreases the Gibbs free energy of the electrode reaction. However, the reverse is the case in case of water + ethylene glycol and water + acetone mixtures. Here the E° values decrease with increase in ethylene glycol or acetone content because the dielectric constant of the mixtures decreases with the increase in the organic solvent content.

The standard transfer thermodynamic quantities

(ΔG_t° ΔH_t° and ΔS_t°) for the process,

SO_4^{2-}(in water)-->SO_4^{2-}(in mixed solvent),

have been evaluated at different temperatures for various solvents. These quantities on the mole fraction basis at 25°C are shown in Table 3. It is known that the Gibbs free energy of transfer is an important index of the differences in interactions of the ions and solvent molecules in two different media. As can be seen from the Table 3, the values of the ΔG_t° for the transfer of SO_4^{2-} ions from water to water + urea mixtures appear to

be negative and become increasingly negative with increase in urea content The negative values of ΔG_t° indicate that the transfer of SO_4^{2-} ions from water to water + urea mixtures is favorable. Thus SO_4^{2-} ions appear to be in a lower Gibbs energy state and hence, more strongly stabilised in water + urea mixtures. The positive values of ΔG_t°, with the increase in the organic solvent content of the water + ethylene glycol or water + acetone mixtures is not favourable and the SO_4^{2-} + ions appear to be in higher Gibbs energy state in these mixed solvents. The negative values of ΔH_t° and ΔS_t° for all the solvents suggest that the transfer process is exothermic and the SO_4^{2-} ions are in a greater ordered state in the mixed solvents. However, the disorderdness increases in water + ethylene glycol and water + acetone mixtures as the proportion of the organic solvent increases in the mixed solvents concerned.

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

$$\lim_{N \to 0}(\log {}^{s}f_{w}) = 2\,(\,{}^{w}E_n^\circ - {}^{s}E_N^\circ\,)/2.3026(RT/F)$$

where the limit term indicates the primary medium effect. As the magnitude of this effect indicates the stabilisation of the ion in the solvent concerned, the resulting negative magnitude of this quantity in water + urea mixtures (Table 3) suggest the escaping tendency of the SO_4^{2-} ions is less in water + urea mixtures than in pure water. This is consistent with the conclusion based on the fact that the SO_4^{2-} ions are more strongly stabilised in water + urea mixtures than in aqueous medium. The positive values of the primary medium effect in water + ethylene glycol and water + acetone mixtures suggest that the escaping tendency of the SO_4^{2-} ions is greater in these solvents than in water.

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