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Thermodynamic Studies of Copper(II) Sulfate in Aqueous Mannitol from Electromotive Force Measurements

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Electromotive force measurements of the cell Cu-Hg/$CuSO_4$(m)/Hg_2SO_4(s)/Hg have been made at 288, 298, 308, and 318 K for mannitol composition X=5, 15, and 25% (w/w) in water. The standard emf values of the cell at different temperatures and at different composition of mannitol+water mixtures have been determined by an extrapolation method. These have been utilized to evaluate the mean activity coefficient of copper(II) sulfate. The standard free energy for the cell reaction, and the primary medium effects upon $CuSO_4$ have been evaluated. The standard thermodynamic quantities for the process of transfer of $CuSO_4$ from water to the mannitol solution have been calculated from the values of the standard potential. The transfer parameters have been split into the electrostatic and chemical contributions and the results have been explained in the light of ion-solvent interactions and structural contributions to solvents.

The behavior of electrolytes in aqueous carbohydrate solutions has recently been a subject of interest.[1–6] The study of electrolytes in carbohydrate solutions is of great importance in the understanding of the physiological and biological processes associated with life. Blokhra et al.[7–9] have reported the transfer energetics of copper(II) sulfate in diethylene glycol-water, ethylene glycol-water, dioxane-water mixtures, and urea-water solutions. In continuation with the previous study, the present investigations have been carried out by using copper(II) sulfate in different mannitol+water mixtures. By setting a suitable cell, we carried out electromotive force measurements. The temperature variation of the standard potential was used to calculate different thermodynamic quantities. From these quantities and transfer energetics, we can obtain information about the thermodynamic properties of $CuSO_4$ in these solvents and about the properties and structure of the solvents. The activity coefficients of copper(II) sulfate in various mannitol+water mixtures have also been calculated.

Experimental

Mannitol and copper(II) sulfate were of analytical grade and were used without further purification. Water used was triply distilled having specific conductance of the order of 10^{-14} $m^{-1}\,\Omega^{-1}$. Solvents of various compositions were made by weight.

The emf cell used for the present study was as previously described.[7–9] Copper amalgam was prepared by electrolyzing a copper(II) perchlorate solution with a mercury pool as cathode, as described elsewhere.[10] At room temperature, a two-phase amalgam is formed between 0.0032 and 24.1% copper (w/w).[11,12] Within this range the potential will be independent of composition, and the exact composition of copper is therefore unimportant.[13] All precautions taken earlier[7] were observed in the present investigation as well.

The emf measurements were made with a digital potentiometer (Equip Tronics, Bombay) having precision of ±0.1 mV. All measurements were made in water thermostat having fluctuation of <±0.1 °C. The cell attained equilibrium after about one hour in all the solvent mixtures. The concentrations of the solutions were occassionally checked with a conductivity bridge and no significant change was detected.

Results and Discussion

The emf (E) values of the cell are reported in Table 1.

Table 1. Electromotive Force Measurements of the Cell Used (E/V) in Various Mannitol+Water Mixtures at Different Temperatures

Concentration	T/K			
10^{-3} mol kg^{-1}	288	298	308	318
	5% mannitol			
4.00	0.4078	0.4070	0.4048	0.4038
6.00	0.4068	0.4048	0.4030	0.4018
8.00	0.4038	0.4028	0.4018	0.4010
10.00	0.4018	0.4010	0.3988	0.3978
20.00	0.3938	0.3918	0.3898	0.3878
40.00	0.3858	0.3828	0.3798	0.3768
60.00	0.3820	0.3788	0.3758	0.3718
80.00	0.3788	0.3748	0.3718	0.3688
100.00	0.3768	0.3730	0.3688	0.3658
	15% mannitol			
4.00	0.4068	0.4048	0.4020	0.3998
6.00	0.4028	0.4008	0.3988	0.3968
8.00	0.4010	0.3990	0.3968	0.3948
10.00	0.3988	0.3968	0.3948	0.3918
20.00	0.3888	0.3868	0.3848	0.3828
40.00	0.3840	0.3818	0.3788	0.3758
60.00	0.3788	0.3758	0.3728	0.3698
80.00	0.3758	0.3730	0.3698	0.3668
100.00	0.3728	0.3698	0.3668	0.3640
	25% mannitol			
4.00		0.4018	0.3990	0.3968
6.00		0.3978	0.3958	0.3938
8.00		0.3948	0.3928	0.3908
10.00		0.3920	0.3898	0.3878
20.00		0.3848	0.3818	0.3788
40.00		0.3798	0.3768	0.3748
60.00		0.3738	0.3718	0.3688
80.00		0.3698	0.3678	0.3648
100.00		0.3678	0.3648	0.3620

Assuming copper(II) sulfate to be dissociated in the solutions studied, the standard molal potentials, $E_m^\ominus$, of the cell:

$$\text{Cu-Hg}/\text{CuSO}_4(\text{m}),\ \text{mannitol} + \text{water mixtures}/\text{Hg}_2\text{SO}_4(\text{s})/\text{Hg}$$

in different solutions have been estimated satisfactorily from the Hitchcock[14] type equation because concentration of solutions is <0.1 m.

$$E_o' = E + k\log m - k\left(\frac{AZ^+Z^-I^{1/2}}{1+Ba_oI^{1/2}}\right) = E_m^\ominus - kB'I, \quad (1)$$

where I is the ionic strength of the solution, m is the molal concentration of the solution, A and B are the Debye–Hückel constants, a_o is the ion-size parameter, Z^+ and Z^- are the valencies of the cation and anion, respectively, and k equals $2.3026\ RT/F$. B' is a constant quantity and it is a measurement of the interaction energy.[14] For each solvent at any temperature $E_m^\ominus$ was obtained by the usual extrapolation technique and the procedure is essentially the same as that used in our previous determinations.[7–9]

The dielectric constant (D_s) for the various mannitol + water mixtures were taken from the literature.[15] The densities (ρ_o) and the Debye parameters were determined experimentally[16] and from the expressions given in standard electrochemistry book.[17] The parameters A, B, and D_s are given in Table 2.

The values of activity coefficients, $\lambda_\pm$, can be evaluated from the relation.[18]

$$E = E_m^\ominus - k\log m\lambda_\pm. \quad (2)$$

From Eq. 1 it is expected that E_o' should be linear function of I when a suitable value of the ion-size parameter is chosen. The intercept of the plot at I=0 gives the value of $E_m^\ominus$. The a_o values for the various solvent mixtures at different temperatures are chosen in such a way that the deviation from linearity of the plot of E_o' against I is minimum. The following a_o values were selected for the different mannitol + water mixtures:

Mannitol (wt%)	5	15	25
a_o/Å	5.0	5.1	5.2

The values of $E_m^\ominus$ have average standard deviation of ±0.3 mV, these values at different temperatures for various mannitol + water mixtures are given in Table 3. The values of $E_m^\ominus$ could be expressed as a function of temperature in the following form:

$$E_m^\ominus = a - b(T-298.15) - c(T-298.15)^2, \quad (3)$$

where T is the temperature in K. The constants a, b, and c are given in Table 4.

The mean activity coefficient $\lambda_\pm$ of copper(II) sulfate

Table 2. Parameters for the Evaluation of E_o' in Mannitol + Water Mixtures at Different Temperatures

T/K	D_s	A/mol$^{-1/2}$ kg$^{1/2}$	10^{-10} B/m^{-1} mol$^{-1/2}$ kg$^{1/2}$
		5% mannitol	
288	81.35	0.509	0.329
298	77.83	0.517	0.330
308	74.23	0.529	0.333
318	70.80	0.540	0.335
		15% mannitol	
288	79.95	0.522	0.331
298	76.30	0.532	0.334
308	72.70	0.545	0.336
318	69.10	0.568	0.341
		25% mannitol	
298	74.77	0.549	0.336
308	71.05	0.564	0.339
318	67.55	0.580	0.343

Table 4. Values of the Constants a, b, c in Eq. 3

Mannitol/wt%	a/V	b/10^{-4} V K^{-1}	c/10^{-6} V K^{-2}
0	0.2659	7.25	0.00
5	0.2605	6.63	6.25
15	0.2561	6.50	6.25
25	0.2508	7.25	2.50

Table 5. Mean Molal Activity Coefficient of $CuSO_4$ in Various Mannitol + Water Mixtures at 298 K

Concentration	Mannitol (wt%)			
10^{-3} mol kg^{-1}	0	5	15	25
4.00	0.559	0.864	0.760	0.690
6.00	0.509	0.628	0.592	0.537
8.00	0.501	0.509	0.476	0.453
10.00	0.451	0.437	0.415	0.404
20.00	0.333	0.313	0.307	0.267
40.00	0.236	0.222	0.186	0.163
60.00	0.191	0.173	0.157	0.137
80.00	0.168	0.152	0.131	0.120
100.00	0.151	0.130	0.119	0.104

Table 3. Standard Molal Potentials of the Cell Used in Mannitol + Water Mixtures at Various Temperatures (The Values in Parentheses are Calculated from Constants a, b, and c of Eq. 3)

Mannitol	$E_m^\ominus$/V			
wt%	288 K	298 K	308 K	318 K
0	0.2730 (0.2732)	0.2655 (0.2660)	0.2585 (0.2587)	0.2515 (0.2514)
5	0.2655 (0.2665)	0.2615 (0.2615)	0.2540 (0.2533)	0.2470 (0.2449)
15	0.2620 (0.2620)	0.2560 (0.2560)	0.2490 (0.2490)	0.2405 (0.2419)
25	—	0.2505 (0.2505)	0.2435 (0.2434)	0.2350 (0.2358)

in different solvent was calculated with the help of Eq. 2 and these values at 298 K are listed in Table 5. An error of ±0.1 mV in emf values results in an error of ±0.002 in the value of $\lambda_{\pm}$.

The values of the activity coefficient in water (0% mannitol) are comparable with the literature values[23,24] at 298 K e.g. it is 0.153[23] and 0.150[24] for 0.1 m $CuSO_4$, 0.438[23] for 0.01 m $CuSO_4$, showing thereby that there is consistency in the measurements and the estimation of the molal activity coefficient of copper(II) sulfate. The values of the activity coefficient at a particular molality have been found to decrease with increasing mannitol content in the medium except 4.00, 6.00, and 8.00 m solutions in water. The decrease in the values may be attributed to the lowering of the dielectric constant of the medium and the abnormal lower values at lower concentration in water may be attributed to the increase in the ion–ion interactions or partial hydrolysis of the copper sulfate solution.

The standard thermodynamic function ΔG° for the cell reaction:

$$Hg_2SO_4(s) + Cu\text{-}Hg(s) \rightleftarrows 3\ Hg(s) + CuSO_4\ (\text{solvated})$$

has been calculated from the temperature variation of the standard molal potential in mannitol + water solvent using

$$\Delta G^{\circ} = -nFE^{\circ}_{m} = -2F[a-b\ (T-298.15)-c(T-298.15)^2]. \quad (4)$$

The calculated thermodynamic functions of the cell at 288—318 K in 0, 5, 15, and 25% (w/w) of mannitol + water solvents are recorded in Table 6. It is evident from Table 6 that all the thermodynamic functions are negative. The magnitude of the standard free energy changes increases with an increase in either the mannitol content in the solvent mixture or the temperature of the solvent system which may be attributed to the decrease in the dielectric constant of the medium. As the dielectric constant decreases, more work is required to keep the ions apart, and therefore, less work is produced by the electrode reaction and more positive free energy changes results. There is less spontaneity, because of decrease dissociation at lower dielectric constants.

The primary medium effect represents the difference in ion solvent interaction for copper(II) sulfate at the standard state in the particular solvent and in water. It is a measure of the change of Gibbs free energy which accompanies the transfer of one mole of copper(II) sulfate from the standard state in water to the standard state in respective solvent. Thus the primary medium effect measures the change in escaping tendency of copper(II) sulfate in the transfer from a standard state in one solvent to a standard state in another solvent. The primary medium effect, log ${}_{w}^{s}\gamma_{\pm}^{\circ}$ (mole fraction scale), of the mannitol + water solvents upon $CuSO_4$ were computed by the usual relation[19,20] at 288—318 K. The results are given in Table 7. It is seen from Table 7 that addition of mannitol changes the behavior of the medium upon the ions and the effect upon the ions is greater at higher concentrations of mannitol. Further it shows a decreasing tendency with increasing temperature. This suggests that the escaping tendency of $CuSO_4$ is greater in mannitol + water solvents than in water.

The standard thermodynamic quantities for the transfer of one mole of copper(II) sulfate from the standard state in water (w) to the standard state of respective solvents (s) were evaluated at 288—318 K with the help of usual relations.[19,20]

$$-2F[(E_m)_s-(E_m)_w] - 2\times 2.3026RT\log(M_s/M_w) = \Delta G^{\circ}_{t} = O - PT + QT^2 \quad (5)$$

and the corresponding values for solutions of copper(II) sulfate in the various solvent media at 288—318 K are given in Table 8.

It is quite evident from Table 8 that the standard Gibbs free energy of transfer, ΔG°_{t}, becomes more and more positive with the increase of mannitol content in the medium. The positive ΔG°_{t} values suggest that the electrolyte is in higher free energy state in mannitol + water mixtures than in water so that copper(II) sulfate has more affinity for water than mannitol + water mixtures. The transfer of copper(II) sul-

Table 6. Standard Molal Free Energy of the Cell Reaction in Various Mannitol + Water Solvents at 288—318 K

T/K	Mannitol/wt%			
	0	5	15	25
	$-\Delta G^{\circ}$/kJ mol^{-1}±0.020			
288	52.69	51.24	50.57	—
298	51.24	50.47	49.41	48.35
308	49.89	49.02	48.06	46.99
318	48.54	47.67	46.42	45.36

Table 7. Primary Medium Effect, log${}_{w}^{s}\gamma_{\pm}^{\circ}$ (Mole Fraction Scale), of Mannitol + Water Solvents upon $CuSO_4$ at 288—318 K and the Values of the Constants O, P, and Q of Eq. 5 for Evaluation of Thermodynamic Quantities for Transfer of $CuSO_4$ from Water to Mannitol + Water Media

Mannitol	log${}_{w}^{s}\gamma_{\pm}^{\circ}$				$O\times10^{-3}$	$P\times10^{2}$	Q
wt%	288 K	298 K	308 K	318 K	J mol^{-1}	J K^{-1} mol^{-1}	J K^{-2} mol^{-1}
5	0.0656	0.0381	0.0368	0.0357	135.890	8.910	1.4450
15	0.0963	0.0846	0.0777	0.0872	113.441	7.366	1.2075
25	—	0.1311	0.1228	0.1308	91.738	5.905	0.9675

Table 8. Standard Thermodynamic Quantities for the Transfer of Copper(II) Sulfate from Water to Mannitol + Water Mixtures at Various Temperatures

T/K	Mannitol/wt%		
	5	15	25
	$\Delta G^\ominus_t$/kJ mol^{-1}		
288	1.15	1.46	—
298	0.71	1.17	1.68
308	0.56	1.13	1.64
318	0.70	1.32	1.79
	$\Delta H^\ominus_t$/kJ mol^{-1}		
288	18.03	13.29	—
298	9.56	6.21	5.82
308	0.81	−1.11	−0.43
318	−8.24	−8.67	−6.10
	$\Delta S^\ominus_t$/J K^{-1} mol^{-1}		
288	58.60	41.05	—
298	29.70	16.90	13.90
308	0.80	−7.25	−5.45
318	−28.10	−31.40	−24.00
	$-\Delta C_p$/J K^{-1} mol^{-1}		
288	832	696	—
298	861	720	576
308	890	744	596
318	919	768	615

fate from water to mannitol + water mixture is, therefore, not a spontaneous process with the solute in standard state in either medium. Ahluwalia and Sharma[21] suggested that the transfer of structure breaking solutes should be accompanied by a positive free energy change thereby making the transfer of there solutes from water to the mixed solvents thermodynamically unfavorable. The positive $\Delta G^\ominus_t$ values, therefore suggests that copper(II) sulfate behaves as a structure breaker in water. The positive $\Delta G^\ominus_t$ values also suggest that water is more basic than mannitol + water solvents and basicity decreases with increasing the mannitol concentration in the solvents. This view is also consistant with the fact that the escaping tendency of copper(II) sulfate is greater in mannitol + water solvent than in the pure aqueous solutions (Table 7, medium effect). The effect of temperature on $\Delta G^\ominus_t$ shows decrease in the contribution for the effects of the ions on the structure of the solvents.

The values of the transfer entropy and enthalpy reflect the complicated nature with regard to the contributions from the effects of the ions on the structure of the solvents. The values of $\Delta H^\ominus_t$ and $\Delta S^\ominus_t$ are negative at 318 K and at 15% and 25% mannitol at 308 K, while values at other temperatures and concentration are positive. The negative values suggest that the tendency of order created by copper(II) sulfate in 15% and 25% mannitol + water mixtures at 308 K and 5%, 15%, and 25% mannitol + water mixtures at 318 K is more than in pure water. However this tendency is less in 5% (w/w) mannitol + water mixture at 308 K and in all the solvents at 288 and 298 K in comparison with pure water. This shows reintroduction of some order in mannitol + water mixtures at higher temperatures. Copper(II) sulfate thus breaks more structure in water than in mannitol + water solvent at higher temperatures.

The process of transfer is associated with the transfer of charged species i.e. Cu^{2+} and SO_4^{2-} ions from water to the aqueous mannitol medium. It may, therefore, be possible to split the $\Delta G^\ominus_t$ values into two parts as suggested earlier[22] an electrostatic part, $\Delta G^\ominus_{t,el}$ corresponding to a change in dielectric constant of the medium, and a nonelectrostatic or chemical part, $\Delta G^\ominus_{t,ch}$, arising from specific chemical interactions between the ions and the solvent. Thus

$$\Delta G^\ominus_t = \Delta G^\ominus_{t,el} + \Delta G^\ominus_{t,ch}. \qquad (6)$$

The electrostatic contribution $\Delta G^\ominus_{t,el}$, $\Delta H^\ominus_{t,el}$, $\Delta S^\ominus_{t,el}$, and the chemical contributions $\Delta G^\ominus_{t,ch}$, $\Delta H^\ominus_{t,ch}$, $\Delta S^\ominus_{t,ch}$ have been calculated as described earlier.[7–9] These values so calculated at 298 K are presented in Table 9. It is obvious from Table 9 that $\Delta G^\ominus_{t,ch}$ and $\Delta G^\ominus_{t,el}$ are increasingly positive in all mannitol + water mixtures. This indicates that transfer of $CuSO_4$ from water to mannitol + water mixtures is not favored as far as chemical interactions are concerned. This suggests that all mannitol + water mixtures are less basic than pure water and this enhances with increasing mannitol concentration. The electrostatic contribution of enthalpy and entropy of transfer goes on decreasing with increase in mannitol concentration. Same is the trend for chemical contribution. Taking an overall view it can be inferred that the chemical contribution or solvation predominates over electrostatic factor, resulting in an overall unfavorable effect on the transfer process from water to mannitol + water mixtures. The negative values of these parameters may be due to the introduction of order in mannitol + water mixtures.

Table 9. Electrical and the Chemical Parts of the Thermodynamic Quantities Accompanying the Transfer of Copper(II) Sulfate from Water to Mannitol + Water Mixtures at 298 K

Mannitol	$\Delta G^\ominus_{t,el}$	$\Delta G^\ominus_{t,ch}$	$\Delta H^\ominus_{t,el}$	$\Delta H^\ominus_{t,ch}$	$\Delta S^\ominus_{t,el}$	$\Delta S^\ominus_{t,ch}$
wt%	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}
5	0.094	0.62	0.092	9.47	−1.75	31.45
15	0.410	0.76	−1.622	7.83	−6.82	23.72
25	0.738	0.94	−1.884	7.70	−8.80	22.70

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