# Thermodynamic Properties of Solutions of Copper Sulphate in Ethylene Glycol & Aqueous Ethylene Glycol

R. L. BLOKHRA & Y. P. SEHGAL

Department of Chemistry, Himachal Pradesh University, Simla 171005

Activity coefficients of copper sulphate in water, ethylene glycol (EG) at 30°, 35° and 40° and in 20, 50 and 80% (by wt) ethylene glycol-water mixtures at 30°, have been calculated at different [electrolyte], from the e.m.f. of the cell of the type:

Cu(electroplated)/CuSO₄(c)/Hg₂SO₄(s)/Hg
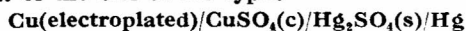
Standard free energy transfer, ΔG^0_{tr}, from water to aq. EG and from EG to aq. EG has also been calculated from the E^0 values of the cell. The chemical part of the standard free energy of transfer has been estimated from Born's equation and the results are discussed in terms of the solute-solvent interactions.

THOUGH thermodynamic properties of some uni-univalent electrolytes in glycols have been reported[1-9], very little work has been done on the thermodynamic properties of 2:2 electrolytes in non-aqueous and in mixed solvents. Blokhra *et al.*[10] have recently reported the thermodynamic properties of $CuSO_4$ in diethylene glycol and aqueous diethylene glycol.

Since copper ions are very good oxidizing/reducing agents, the present investigations have been carried out with a view to determining (i) the activity coefficient of $CuSO_4$ in ethyleneglycol (EG) and in its aqueous mixtures, and (ii) free energy of transfer from EG to aq. EG, and also from H_2O to aq. EG.

Materials and Methods

Ethylene glycol (BDH) was purified by distillation under reduced pressure after drying it over calcium oxide, calcium-sulphate and stored in sealed bottles. The density (1·10982 g ml⁻¹), viscosity ($\eta_0 = 0·170$ poise) and specific conductance (8×10^{-7} ohm⁻¹ cm⁻¹) of the purified EG at 25° are in good agreement with the literature values[11].

Copper sulphate (AR) was used as such. Water of specific conductance $1·3 \times 10^{-6}$ ohm⁻¹ cm⁻¹ was used for the preparation of the aqueous mixtures (by weight) of EG.

The cell (A) used in the study consisted of a cell tube of pyrex glass (length 9 in., int. diam. 1 in.), at the bottom of which a platinum wire was fixed. Contact of the platinum wire inside the cell tube was covered with $Hg/Hg_2SO_4/CuSO_4$(c). The electroplated copper electrode was dipping inside the copper sulphate solution.

[Cu(electroplated)/CuSO₄(c)/Hg₂SO₄(s)/Hg]

(A)
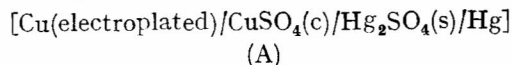
The procedure for the preparation of electroplated copper electrodes was the same as described in our earlier publication[10]. Two sets of copper electrodes

were made at a time and the electrodes prepared had stable asymmetric potential of 0·1 mV. Further the system was closed and the electrodes were never exposed to the atmosphere to avoid oxidation.

The e.m.f. measurements were made with OSAW (Ambala) precision potentiometer having an accuracy of ±0·1 mV. A dc spot galvanometer was used in conjunction with the potentiometer. All measurements were made in an air-thermostat having temperature fluctuations less than ±0·02°.

The equilibrium of the cell was attained after 30 to 40 min. The constant e.m.f. was recorded and was used in the further calculations.

Results and Discussion

The e.m.f. data in water, pure EG and its aqueous mixtures as a function of concentration and temperature are given in Tables 1 and 2 respectively.

The e.m.f. for all the systems at various temperatures (Tables 1 and 2) decreases with the increase in [electrolyte]. The e.m.f. of the cell (A) is given by the relation[12]:

$$E_{obs} = E^0 - \frac{RT}{F} \ln C\gamma \qquad ...(1)$$

where the symbols have their usual significance.

The standard e.m.f. (E^0) of the cell (A) in water, EG and aq. EG have been evaluated by Hitchcock[13] type method using Eq. (2)

$$\left[E_{obs} + \frac{RT}{F} \ln C - \frac{2·303RT}{F} \frac{AZ^+Z^-\sqrt{\mu}}{1+\beta\alpha_i^0\sqrt{\mu}} \right]$$
$$= E^0 - \frac{2·303RT}{F}B'\mu \qquad ...(2)$$

where μ is the ionic strength; Z^+, Z^- are the valencies of Cu^{2+} and SO_4^{2-} ions respectively. A and β are the Debye-Hückel constants, B' is a constant quantity and is a measure of interaction energy[14] and α_i^0 is the ion-size parameter in angstrom units.

TABLE 1 — E.m.f. DATA FOR CuSO₄ IN WATER AT
DIFFERENT CONCENTRATIONS AND TEMPERATURES

Conc. (c) M	E_{obs} (V) at			
	25°	30°	35°	40°
	WATER			
0·01	0·416	0·414	0·413	0·410
0·05	0·392	0·391	0·389	0·387
0·08	0·386	0·384	0·382	0·381
0·10	0·385	0·382	0·380	0·378
0·20	0·378	0·373	0·371	0·369

TABLE 2 — E.m.f. DATA FOR CuSO₄ IN EG AND AQ. EG
AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Conc. M	E_{obs} (V)	Conc. M	E_{obs} (V)	Conc. M	E_{obs} (V)
EG; TEMP. 30°		EG; TEMP. 35°		EG; TEMP. 40°	
0·0321	0·122	0·0465	0·108	0·0228	0·114
0·0400	0·118	0·0672	0·100	0·0354	0·106
0·0509	0·114	0·0997	0·092	0·0450	0·100
0·0622	0·112	0·1387	0·086	0·0654	0·092
0·0834	0·106	0·1973	0·080	0·0858	0·086
0·1055	0·100	0·2250	0·078	0·1052	0·080
0·1489	0·096	0·2352	0·076	0·1236	0·074
0·2263	0·092	—	—	—	—
20% EG (30°)		50% EG (30°)		80% EG (30°)	
0·0341	0·234	0·0383	0·210	0·0497	0·178
0·0506	0·228	0·0545	0·204	0·0567	0·174
0·0650	0·224	0·0704	0·197	0·0671	0·171
0·0854	0·216	0·0937	0·192	0·0796	0·169
0·0975	0·214	0·1174	0·187	0·0927	0·166
0·1543	0·207	0·1404	0·184	0·1076	0·163
0·1704	0·205	0·2073	0·178	0·1484	0·158
0·1920	0·203	—	—	0·1926	0·155

TABLE 3 — VALUES OF THE ACTIVITY COEFFICIENTS OF
CuSO₄ IN WATER AT 25°, 30°, 35° AND 40°

Conc. (c) M	Υ at 25°			
	Our work	Ref. 18	Ref. 19	Ref. 20
0·01	0·465	0·438	—	—
0·05	0·237	0·216	0·217	—
0·08	0·187	—	—	—
0·10	0·155	0·153	0·160	0·150
0·20	0·102	0·107	0·110	0·104

Υ at temp.*		
30°	35°	40°
0·436	0·425	0·416
0·210	0·209	0·204
0·172	0·170	0·160
0·148	0·147	0·142
0·105	0·103	0·098

*Present work.

Sum of the ionic radii is given as 3·70 Å (ref. 15)
and 4·17 Å (ref. 16) and in the present investigation
the ion-size parameter, α_i^0, of the Debye-Hückel
relation is chosen as equal to 4 Å for aqueous
solutions of copper sulphate because it gave the

best linear plots of the bracketed term of Eq. (2),
designated as $(E^0)'$ versus μ.

The value of E^0 (0·278 V) for the aqueous solution
of CuSO₄ at 25° obtained from the intercept of the
$(E^0)'$ versus μ plots, is in excellent agreement with
the value (0·277 V) obtained by Lewis and Lacey[17]
with the electroplated electrodes. Values of E^0
for CuSO₄ in water at 30°, 35° and 40° were found
to be 0·272, 0·268 and 0·263 V respectively.

The values of the activity coefficients of CuSO₄
in water at 25°, 30°, 35° and 40° estimated from
Eq. (1) using the above estimated $E°$ values are
given in Table 3. The literature values at 25° are
also included in Table 3.

A fairly good agreement between the observed
values of Υ and the values obtained by other
workers at 25° is noticed.

The experimental results for water as a solvent
are described to justify the technique used for the
evaluation of E^0 and Υ values in EG and aq. EG,
and for estimating the free energy of transfer from
H₂O to EG.

The Debye-Hückel parameters A and β for EG
and EG-H₂O mixtures, estimated from the data of
Kundu et al.[5], are given in Table 4.

The ion-size parameter, α_i^0, of the Debye-Hückel
relation is chosen as equal to 5 Å, because it gave
the best linear plots of $(E^0)'$ versus μ for EG and
aq. EG solutions of CuSO₄. The values of $E°$ at
30° estimated for aqueous solutions of EG contain-
ing 20, 50 and 80% (by wt) are 0·115, 0·086 and
0·043 V respectively. The values of E^0 in ethy-
leneglycol at 30°, 35° and 40° are −0·043, −0·055
and −0·056 respectively. The data show that
with the increase in the ethylene glycol content,
E^0 values decrease. The values of E^0 for solutions
in EG are negative at all temperatures. This is
not unexpected, since negative values of E^0 of Ag-
AgBr in HBr solutions in EG and of Ag-AgCl in
HCl solutions in methanol-acetonitrile have been
reported by Kundu et al.[21] and Benetto et al.[22],
respectively.

Small variations in the value of α_i^0 have no
detectable influence on the value of E^0. Further,
at very low concentrations of CuSO₄ solutions, the
e.m.f. values are not measurable with a sufficient
degree of accuracy, and therefore, the agreement
between the observed Υ for CuSO₄ in water at 25°
at 0·05M (Table 3) is not as good as observed at
higher concentrations.

The activity coefficients, Υ, of CuSO₄ in EG and
aq. EG mixtures at different temperatures were

TABLE 4 — DEBYE-HÜCKEL CONSTANTS OF EG AND
EG-H₂O MIXTURES

Solvent	Temp. (°C)	ϵ_s	A	$\beta \times 10^{-8}$
100% EG	30	36·74	1·557	0·4782
	35	35·80	1·579	0·4805
	40	34·89	1·602	0·4828
20% EG	30	71·50	0·579	0·3440
50% EG	30	61·50	0·718	0·3696
80% EG	30	47·50	1·059	0·4206

calculated from Eq. (1). The values of γ at rounded concentrations were computed from the γ versus C plots using the interpolated data. These values are given in Tables 5 and 6 respectively.

Data in Tables 5 and 6 indicate that in EG and EG-H₂O solutions of CuSO₄ at all concentrations, the activity coefficient decreases with increase in [electrolyte]. Also, activity coefficient decreases with the increasing proportion of EG in aq. EG mixtures i.e. with decreasing dielectric constant of the solvent. This is expected from the Debye-Hückel theory.

The higher magnitude of activity coefficients in EG-H₂O mixtures than in EG suggests that solute-solvent interaction is more in aq. EG than in pure EG. Also, the activity coefficient of CuSO₄ in EG at 40° are higher than at 30° and 35°. This again may be attributed to the greater solute-solvent interactions at 40° than at 30° and 35°.

The standard free energy of transfer, $\Delta G^0_{tr.}$ of CuSO₄ from H₂O to EG and from EG to aq. EG have been evaluated from Eq. (3)

$$\Delta G^0_{tr.} = F[E^0_N(\text{water}) - E^0_N(\text{solvent})] \qquad \ldots(3)$$

The values of $\Delta G^0_{tr.}$, from EG to aq. EG, of CuSO₄ in aq. EG containing 20, 50 and 80% (by wt) of EG are -3.64, -2.98 and -1.98 kcal mol⁻¹ at 30°. In pure EG, the values of $\Delta G^0_{tr.}$ of CuSO₄ from H₂O to EG are 7.27, 7.45 and 7.36 kcal mol⁻¹ at 30°, 35° and 40° respectively.

The negative values of $\Delta G^0_{tr.}$, for the transfer of CuSO₄ from EG to aq. EG suggests that this transfer is thermodynamically favourable. The positive, $\Delta G^0_{tr.}$ values for the transfer of CuSO₄ from H₂O to EG suggest that this transfer is thermodynamically unfavourable.

The transfer process is associated with the transfer of charged species, i.e. Cu²⁺ and SO₄²⁻ ions from H₂O to aq. EG and from EG to aq. EG. It is therefore plausible to expect that it consists of an electrostatic part, ΔG^0_t (el.), corresponding to a change in the dielectric constant of the medium, and another non-electrostatic part, ΔG^0_t (nonel.) arising from the specific chemical interactions between the ions and the solvent and is therefore solvent-dependent. Thus:

$$\Delta G^0_{tr.} = \Delta G^0_t(\text{el.}) + \Delta G^0_t (\text{nonel.}) \qquad \ldots(4)$$

The electrostatic part of the standard free energy of transfer, ΔG^0_t (el.) has been calculated in EG and EG-H₂O mixtures from Born's[23] Eq. (5)

$$\Delta G^0_t(\text{el.}) = \left(\frac{Ne^2}{2}\right)\left(\frac{1}{\gamma^+} + \frac{1}{\gamma^-}\right)\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right) \qquad \ldots(5)$$

where N is the Avogadro's number, e is the electronic charge (in esu), γ^+ and γ^- are the radii of the Cu²⁺ and SO₄²⁻ ions ($\gamma^+ = 1.28$ Å and $\gamma^- = 2.89$ Å), ϵ_s and ϵ_w are the dielectric constants of the solvent (EG or EG-H₂O, as the case may be) and of water respectively. Thus substituting the various quantities in RHS of Eq. (5), ΔG^0_t (el.) was estimated. ΔG^0_t (nonel.) was then evaluated from Eq. (4). The values of ΔG^0_t (el.) and ΔG^0_t (nonel.) obtained are given in Table 7.

ΔG^0_t (nonel.) is increasingly negative when it is evaluated for the transfer process involving EG to

TABLE 5 — ACTIVITY COEFFICIENT (γ) OF CuSO₄ IN EG AT ROUNDED CONCENTRATIONS

Conc. (c) M	γ at temp.		
	30°	35°	40°
0.01	0.072	0.070	0.095
0.02	0.062	0.060	0.084
0.03	0.057	0.054	0.076
0.04	0.053	0.048	0.073
0.05	0.050	0.045	0.069
0.06	0.048	0.041	0.066
0.08	0.042	0.042	0.062
0.10	0.039	0.035	0.061
0.12	0.035	0.034	0.060
0.16	0.030	0.030	0.060
0.18	0.029	0.028	—
0.20	0.027	0.026	—

TABLE 6 — ACTIVITY COEFFICIENT (γ) OF CuSO₄ IN EG-H₂O MIXTURES AT 30°

Conc. (c) M	γ in aq. EG containing EG (% by wt)		
	20	50	80
0.01	0.340	0.296	0.165
0.02	0.312	0.262	0.147
0.03	0.292	0.240	0.135
0.04	0.276	0.228	0.126
0.05	0.264	0.216	0.119
0.06	0.256	0.208	0.112
0.08	0.238	0.182	0.102
0.10	0.224	0.174	0.095
0.12	0.210	0.160	0.088
0.16	0.190	0.154	0.077
0.18	0.184	0.150	0.073
0.20	0.178	0.146	0.070

TABLE 7 — VALUES OF ΔG_t^0 (el.) AND ΔG_t^0 (nonel.) FOR THE TRANSFER OF CuSO₄ FROM H₂O TO EG AND EG TO AQ. EG

% EG (by wt)	Temp. (°C)	ΔG_t^0(el.) (kcal mol⁻¹)	ΔG_t^0(nonel.) (kcal mol⁻¹) H₂O → EG	ΔG_t^0(nonel.) (kcal mol⁻¹) EG → aq. EG
20	30	0.08	—	-4.67
50	30	0.25	—	-3.87
80	30	0.63	—	-2.46
100	30	1.11	6.16	—
	35	1.15	6.30	—
	40	1.18	6.18	—

aq. EG. This indicates that the transfer of CuSO₄ from EG to aq. EG is favoured as far as the chemical interactions are concerned, and this also suggests that EG-H₂O mixtures are more basic than pure EG. The ΔG_t^0 (nonel.) values for the transfer process of CuSO₄ from H₂O to aq. EG are increasingly positive suggesting this transfer as unfavourable as far as the chemical interactions are concerned.

Acknowledgement

References

1. KUNDU, K. K., RAKSHIT, A. K. & DAS, M. N., *Electrochim. Acta*, **17** (1972), 1921.
2. SEN, U., KUNDU, K. K. & DAS, M. N., *J. phys. Chem.*, **71** (1967), 3665.
3. KUNDU, K. K., DE, A. L. & DAS, M. N., *J. chem. Soc., Dalton Trans. I*, (1972), 381.
4. KUNDU, K. K. & DAS, M. N., *Electrochim. Acta*, **18** (1973), 95.
5. KUNDU, K. K., JANA, D. & DAS, M. N., *J. phys. Chem.*, **74** (1970), 2625.
6. BANERJEE, S. K., KUNDU, K. K. & DAS, M. N., *J. chem. Soc.* (A), (1967), 166.
7. DAS, M. N. & KUNDU, K. K., *J. Indian chem. Soc.*, **11** (1974), 266.
8. KUNDU, K. K., *Indian J. Chem.*, **11** (1973), 290.
9. SEN, U., *J. chem. Soc. Faraday Trans. I*, (1973), 2006.
10. BLOKHRA, R. L., SEHGAL, Y. P. & KUTHIALA, V. K., *Electrochim. Acta*, **21** (1976), 1079.
11. LANGE, N. A., *Handbook of chemistry* (McGraw-Hill, New York), 1967, 1221, 1233, 1671.
12. MACINNES, D. A., *The principles of electrochemistry* (Dover Publications, New York), 1967, 165.
13. HITCHCOCK, D. I., *J. Am. chem. Soc.*, **20** (1928), 2076.
14. IVES, D. J. G. & JANZ, G. J., *Reference electrodes* (Academic Press, New York), 1961, 38.
15. HUHEEY, J. E., *Inorganic chemistry, principles, structures and reactivity* (Harper & Row, New York), 1962, 77.
16. WELLS, A. F., *Structural inorganic chemistry* (Clarendon Press, Oxford), 1962.
17. LEWIS, G. N. & LACEY, W. N., *J. Am. chem. Soc.*, **36** (1914), 804.
18. GETMAN, F. H., *J. phys. Chem.*, **34** (1930), 154.
19. LATEMER, W. M., *Oxidation potentials* (Prentice-Hall, New York), 1952.
20. ROBINSON, R. A. & STOKES, R. H., *Electrolytic solutions* (Butterworths, London), 1955, 502.
21. KUNDU, K. K., BANERJEE, S. K. & DAS, M. N., *J. chem. Soc.* (A), (1967), 161.
22. BENNETTO, H. P. & SPITZER, M. M., *J. chem. Soc. Faraday Trans. I*, (1973), 1492.
23. BORN, M., *Z. phys.*, **1** (1920), 45.