

CONDUCTIVITIES AND IONIC ASSOCIATION OF COPPER (II) AND MANGANESE (II) SULPHATES IN METHANOL + WATER AT 298.15 K

M. SADIQ KHAN NIAZI

Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan

(Received June 7, 1993; revised November 14, 1993)

Electrolytic conductivities for copper (II) and manganese (II) sulphates in binary mixtures of methanol + water have been measured at 298.15 K. The data were analyzed with the Lee and Wheaton conductivity equation for the derivation of limiting molar conductivities and association constants. The results are compared with those in the literature pertaining to analogous media, derived conductometrically.

Key words: Copper sulphate, Manganese sulphate, Methanol + water mixtures, Conductivities.

Introduction

There have been numerous conductometric studies on 1:1 electrolytes in pure as well in binary mixed solvent systems [1-4]. The literature survey shows that the conductivity measurements on 2:2 salts, especially transition metal (II) sulphates, in mixed solvent systems are rare [5-9].

Present paper reports the molar conductivities for dilute solutions of copper sulphate and manganese sulphate in binary mixtures of methanol with water ranging in composition from 0 to 56.7 mole % of the cosolvent at 298.15 K. The values of limiting molar conductivities, Λ_o , and association constants, K_A , were derived from the concentration-conductivity data and are discussed in terms of solvent effect on these parameters. In addition, results are compared with those available in the literature pertaining to analogous media and the electrolytes.

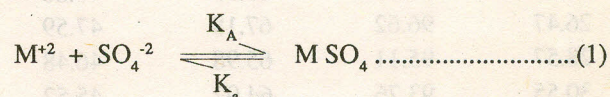
Experimental

Copper sulphate penta hydrate and manganese sulphate mono hydrate were ultra high purity product of Merck (99.8 %) and were recrystallized from triple distilled water. These were dried and stored in a desiccator over P_2O_5 . KCl, also a product of Merck, and was recrystallized from conductivity water, dried for several days in an oven till constant weight was achieved and was stored in a dessicator over P_2O_5 . Methanol (from Merck) and water were distilled and purified as detailed elsewhere [14].

The apparatus and procedure of conductivity measurements were the same as reported earlier [10-13]. The conductivity cell was calibrated with aqueous KCl solutions as recommended as by Wu *et al.* [15]. The values of densities, viscosities and dielectric constants for methanol + water mixtures were taken from previous papers [13-14]. The accuracy of conductance measurement was $\pm 0.1\%$. The temperature of the oil bath was kept at $25 \pm 0.01^\circ$.

Results and Discussion

The molar conductivities, (Λ S-cm² - mol⁻¹), for $CuSO_4$ and $MnSO_4$ solutions of different concentrations in different methanol + water mixtures are given in Table 1. The conductivity - concentration data were analyzed with the Lee and Wheaton conductivity equation [16] in series form as suggested by Pethybridge and Taba [17], for the derivation of the limiting molar conductance, Λ_o , and the association constant, K_A , for the process :



As the data were highly sensitive to ion-pair distance parameter R (called Gurny cosphere diameter [18]), the Λ_o and K_A values, reported in the Table 2, at $R = 6 \text{ \AA}$ for all methanol + water mixtures.

The values of limiting molar conductivities, Λ_o , found for $CuSO_4$ and $MnSO_4$ in aqueous medium are 133.38 and 132.32 S. cm². mol⁻¹ at 298.15 K, respectively. The literature values as quoted by other investigators [5 - 9] are from 133.32 to 134.3 S. cm². mol⁻¹ for $CuSO_4$ and 133.1 S.cm².mol⁻¹ for $NiSO_4$ respectively.

The variation of Λ_o values with composition of methanol + water mixtures and the comparison with the values reported by other research workers [8 - 9] for both salts are shown in Fig.1. The figure indicates that both the electrolytes have different Λ_o values in the same methanol + water mixtures which is in contrast to the Λ_o values found for transition metal (II) salts either 2:1 or 2:2 salts in pure solvents [20 - 25]. The Λ_o values decreased as the contents of methanol increased in the methanol + water mixtures. Further, in the Fig.2, the values of normalized Walden products, i.e. $R^x = (\Lambda_o \eta)^S / (\Lambda_o \eta)^W$, which have been plotted against the inverse dielectric

constant values ($100/\epsilon$) for methanol + water mixtures pass through maximum at about, $x = 0.15$ mole fraction of methanol. These values further infer that the CuSO_4 and MnSO_4 are differently solvated first by the methanol - water clathrate and then by methanol molecules as the contents of methanol increase. Further as seen in the figure, the Λ_0 values found in present work differ with literature values within $\pm 0.5\%$. The difference may be due to the use of different conductivity equation and the parameter R .

The values of association constants, K_A ($\text{dm}^3 \text{ mol}^{-1}$), found for CuSO_4 is 188 ± 0.3 and for MnSO_4 is 181 ± 1 , respec-

tively at 298.15 K and at $R = 6 \text{ \AA}$. As reviewed by the Wasykiewicz [26] the K_A values found by other research worker are 126 to $251 \text{ dm}^3 \text{ mol}^{-1}$ for CuSO_4 and for MnSO_4 are 133 - $200 \text{ dm}^3 \text{ mol}^{-1}$ [7] respectively, depending on the theory and method. The values of K_A increased as the values of R were varied from 4 to 15 \AA . Similar observations were found by other investigators [5 - 8] in aqueous medium. The dependence of $\log K_A$ values on the inverse of dielectric constant values of methanol + water mixtures ($100/\epsilon$) is shown in Fig.3. The non-linearity of the plots indicates some specific short terms interactions of ion with the solvent in addition to simple

TABLE 1. MOLAR CONDUCTIVITIES ($1/2 \Lambda$) FOR METAL (II) SULPHATES IN METHANOL + WATER MIXTURES AT 298.15 K.

$10^4 C/$ ($\text{Mol} \cdot \text{dm}^{-3}$)	$1/2 \Lambda / (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$							
	$x = 0$	5.9	12.3	19.4	27.3	36.0	45.7	56.7
CuSO_4								
3.84	123.11	89.80	72.83	58.39	48.35	37.43	25.38	15.98
7.40	116.86	84.13	65.41	51.57	41.88	31.82	20.89	12.80
10.71	112.10	79.96	60.54	47.27	37.97	28.56	18.45	11.16
13.79	108.30	76.73	57.00	44.22	35.28	26.37	16.85	10.12
16.67	105.17	74.11	54.29	41.92	33.26	24.77	15.71	9.38
19.35	102.54	71.95	52.13	40.11	31.72	23.52	14.84	8.83
21.87	100.29	70.12	50.35	38.63	30.46	22.54	14.16	8.39
24.24	98.33	68.55	48.86	37.40	29.43	21.72	13.60	8.04
26.47	96.62	67.18	47.59	36.36	28.56	21.04	13.13	7.74
28.57	95.11	65.98	46.48	35.46	27.79	20.45	12.74	7.50
30.55	93.76	64.92	45.52	34.68	27.14	19.94	12.40	7.28
32.43	92.54	63.96	44.67	33.99	26.57	19.50	12.10	7.10
34.21	91.43	63.11	43.92	33.38	26.06	19.14	11.84	6.94
35.89	90.44	62.33	43.24	32.83	25.61	18.76	11.61	6.79
37.50	89.52	61.62	42.62	32.34	25.20	18.45	11.40	6.68
MnSO_4								
3.84	125.22	98.48	81.03	66.51	58.46	46.67	31.64	21.11
7.41	119.65	93.14	74.98	59.87	51.73	40.02	26.18	17.05
10.71	115.32	89.12	70.69	55.48	47.46	36.09	23.19	14.92
13.79	111.82	85.94	67.43	52.30	44.43	33.42	21.22	13.56
16.66	108.91	83.34	64.85	49.85	42.15	31.45	19.82	12.59
19.35	106.44	81.16	62.73	47.89	40.35	29.93	18.74	11.86
21.87	104.32	79.30	60.96	46.28	38.87	28.70	17.89	11.28
24.24	102.46	77.69	59.45	44.93	37.65	27.69	17.19	10.82
26.47	100.82	76.29	58.15	43.78	36.61	26.84	16.61	10.44
28.57	99.37	75.05	57.02	42.77	35.72	26.12	16.12	10.11
30.55	98.07	73.94	56.01	41.90	34.94	25.49	15.70	9.84
32.43	96.89	72.95	55.12	41.13	34.25	24.94	15.33	9.58
34.21	95.83	72.06	54.31	40.44	33.64	24.45	15.01	9.37
35.89	94.85	71.25	53.59	39.82	33.09	24.02	14.72	9.18
37.50	93.97	70.51	52.93	39.26	32.60	23.62	14.45	9.01

x : Mole % Methanol.

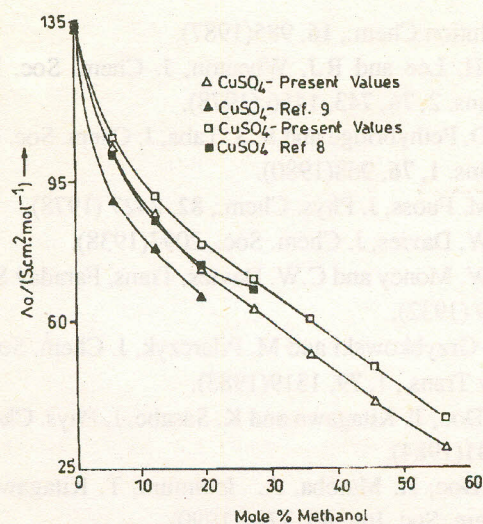


Fig. 1. Comparison of values of limiting molar conductances, Λ_0 , for salts in methanol + water mixtures at 298.15 K.

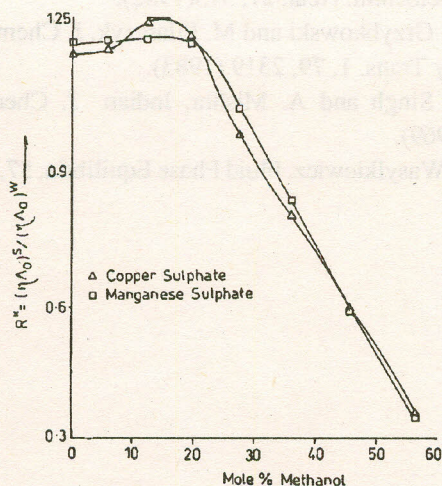


Fig. 2. Dependence of normalized Walden products, $(\Lambda_0\eta)^8 / (\Lambda_0\eta)^W$, values for CuSO_4 and MnSO_4 on the composition of methanol + water mixtures at 298.15 K.

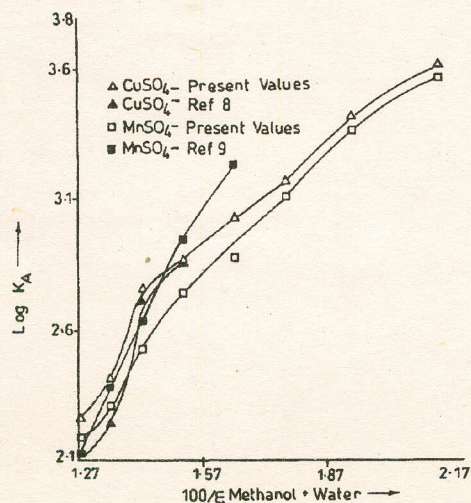


Fig. 3. Dependence of association constant values, $\log K_A$, for CuSO_4 and MnSO_4 on the inverse of dielectric constant values ($1/\epsilon$) for methanol + water mixtures at 298.15 K.

TABLE 2. CONDUCTIVITY PARAMETERS FOR METAL (II) SULPHATES IN METHANOL + WATER MIXTURES AT 298.15 K.

Methanol/ Mole %	$1/2 \Lambda_0 /$ ($\text{S.cm}^2 \cdot \text{mol}^{-1}$)	$K_A /$ ($\text{mol}^{-1} \cdot \text{dm}^3$)	$100\sigma\Lambda / \Lambda_0$ (%)
CuSO_4			
0.0	132.73 ± 0.03	185 ± 0.3	0.02
5.8	98.93 ± 0.02	256 ± 1	0.03
12.3	87.15 ± 0.02	583 ± 3	0.03
19.4	72.86 ± 0.02	776 ± 3	0.02
27.3	63.86 ± 0.01	1072 ± 5	0.03
36.0	52.71 ± 0.02	1457 ± 6	0.02
45.7	41.14 ± 0.03	2550 ± 6	0.01
56.7	30.04 ± 0.02	4129 ± 10	0.01
MnSO_4			
0.0	133.71 ± 0.04	154 ± 1	0.05
5.8	106.77 ± 0.02	204 ± 1	0.03
12.3	91.22 ± 0.03	338 ± 1	0.04
19.4	79.21 ± 0.03	564 ± 2	0.04
27.3	70.55 ± 0.05	763 ± 3	0.05
36.0	63.76 ± 0.03	1275 ± 6	0.03
45.7	49.88 ± 0.02	2329 ± 7	0.02
56.7	37.55 ± 0.05	3655 ± 11	0.06

electrostatic interactions. CuSO_4 has been found more associated in methanol + water mixtures as compared to MnSO_4 . This may be due to smaller size and more polarizability of Cu^{+2} ion as compared to Mn^{+2} ion.

Acknowledgement. Financial support from University Research Fund (URF) is acknowledged gratefully.

References

- G.J. Janz and R.P.T. Tomkins, *Nonaqueous Electrolyte Handbook* (Academic Press, New York, 1972), Vol. I and II.
- R. Fernandez-Prini, *Physical Chemistry of Organic Solvent Systems* (Plenum, London, 1973), Chapter 5.
- V.M.M. Lobo, *Electrolyte Solution* (Universidade de Coimbra, Portugal, 1981 and 1984), Vol. I and II.
- (a) J. Barthel, R. Washter, G. Schmeer and H. Hilbinger, *J. Solution Chem.*, **15**, 531(1986),
(b) J. Barthel, M. Krell, L. Ibrel and F. Feureleih, *J. Electroanal. Chem.*, **214**, 485(1986),
(c) J. Barthel, L. Ibrel, J. Rossmairer, H.J. Gores, and B. Knnkal, *J. Solution Chem.*, **19**, 321(1990).
- B.B. Owen and R.W. Burry, *J. Am. Chem. Soc.*, **60**, 3074(1938).
- W.G. Davies, R.J. Otter and J.E. Prue, *Discuss. Faraday Soc.*, **24**, 103 (1957).

7. (a). K. Kubota, S. Takizawa, W. Kashiwagi and M. Yoko, *Bull. Chem. Soc. Jpn.*, **64**, 2544 (1991).
 (b). S. Katayama, *Bull. Chem. Soc. Jpn.*, **46**, 106(1973).
 (c). H. Yokoyama and H. Yamatara, *Bull. Chem. Soc.*, *Jpn.*, **48**, 2729 (1975).
8. (a) G. Atkinson and S. Petrucci, *J. Am. Chem. Soc.*, **86**, 7(1964) and references cited therein.
 (b). C.J. Hallada and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 3759 (1961).
9. L. Wereblan, A. Balkowska, J. Lesinski, G. Szymanski, C. Borogowska and J. Jastrzebska *Bull. Polish Acad. Sci.*, **39**, 73 (1991).
10. M.S.K. Niazi and A. Khan, *J. Chem. Eng. Data*, **38**, 98(1993).
11. M.S.K. Niazi, I. Jabeen and S.S. Shah, *J. Chem. Eng. Data*, **38**, (1993).
12. M.S.K. Niazi, O. Fischer and E. Fischerova, *J. Solution Chem.*, **15**, 957 (1986).
13. M.S.K. Niazi, *Bull. Chem. Soc. Jpn.*, **62**, 1253 (1989).
14. M.S.K. Niazi and M.Z.I. Khan, *J. Solution Chem.*, **22**, 437 (1993).
15. Y.C. Wu, W.F. Koch, W.H. Hamer and R.L. Kay, *J. Solution Chem.*, **16**, 985(1987).
16. W.H. Lee and R.J. Wheaton, *J. Chem. Soc. Faraday Trans. 2*, **76**, 743, 1456 (1978).
17. A.D. Pethybridge and S. S. Taba, *J. Chem. Soc. Faraday Trans. 1*, **76**, 968(1980).
18. R.M. Fuoss, *J. Phys. Chem.*, **82**, 2427 (1978).
19. C.W. Davies, *J. Chem. Soc.*, 2093(1938).
20. R.W. Money and C.W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).
21. W. Grzybowski and M. Pilarczyk, *J. Chem. Soc. Faraday Trans.*, **1**, **79**, 1319(1983).
22. H. Doe, T. Kitagawa and K. Sasabe, *J. Phys. Chem.*, **88**, 3341(1984).
23. H. Doe, H. Matoba, A. Ichimura, T. Kitagawa, *Bull. Chem. Soc. Jpn.* **63**, 3785(1990).
24. W. Libus, M. Pilarczyk, R. Pastewski and T. Szuchnicka, *Elrctochim. Acta*, **27**, 573(1982).
25. W. Grzybowski and M. Pilarczyk, *J. Chem. Soc. Faraday Trans. 1*, **79**, 2319 (1983).
26. D. Singh and A. Mishra, *Indian J. Chem.*, **7**, 1219 (1969).
27. S. Wasylkiewicz, *Fluid Phase Equilibria*, **57**, 277 (1990).