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Conductivities and Ionic Association of Copper(II) and Manganese(II) Sulfates in Ethanol + Water at 298.15 K

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Electrolytic conductivities for copper(II) and manganese(II) sulfates in ethanol + water, ranging in mole fraction of ethanol from 0 to 0.28, have been measured at 298.15 K. The limiting molar conductivity, Λ_0, and association constant, K_A, were derived from concentration–conductivity results with the Lee and Wheaton conductivity equation. The results are discussed on the basis of the solvent effect on the conductivity parameters of these salts.

Introduction

Though a number of conductivity measurements have been made on transition-metal(II) sulfates in aqueous media (*1–4*), few conductivity measurements in mixed solvent systems have been reported in the literature (*5–9*). The present paper resports molar conductivities of copper(II) and manganese(II) sulfates in ethanol + water, ranging in composition from 0 to 28 mol % ethanol, at 298.15 K. The limiting molar conductivities, Λ_0, and association constant, K_A, were derived from the results and are discussed in terms of the solvent effect on these parameters as the composition of water + cosolvent mixtures is varied.

Experimental Section

Copper sulfate pentahydrate and manganese sulfate monohydrate were ultrahigh-purity products of Merck (99.8 mass %) and were recrystallized with conductivity water and dried in an oven. These were stored in a desiccator over P_2O_5. KCl was also a product of Merck and was recrystallized from conductivity water, dried for several days in an oven till constant mass was achieved, and stored in a desiccator over P_2O_5. The ethanol (Merck) and water were distilled and purified as detailed elsewhere (*10*).

The conductivities were measured with a microprocessor conductivity meter, Model 2000 LF (WTW, Germany), which works at a frequency of 1 kHz with an accuracy of ±0.01% in the conductivity. The temperature of the oil bath was kept constant at 25 ± 0.01 °C. The cell constants 0.986 ± 0.001 and 0.755 ± 0.001, cm^{-1} were obtained by calibration with aqueous KCl solutions as recommended by Wu *et al.* (*11*). The electrodes were platinized black platinum. The densities, viscosities, and dielectric constants for ethanol + water were taken from previous papers (*10, 12, 14*). The other procedures were the same as detailed elsewhere (*13*).

Results and Discussion

The molar conductivities, for $CuSO_4$ and $MnSO_4$ solutions of different concentrations in ethanol + water, are given in Table 1. The dependence of conductivity on concentration was analyzed with the Lee and Wheaton conductivity equation (*15*) as suggested by Pethybridge and Taba (*16*), for the derivation of the limiting molar conductance, Λ_0, and the association constant, K_A, for the process

$$M^{2+} + SO_4^{\ 2-} \underset{K_a}{\overset{K_A}{\rightleftharpoons}} MSO_4 \qquad (1)$$

Table 1. Molar Conductivities (Λ) for Metal(II) Sulfates in *x* Ethanol + 1 − *x* Water Mixtures at 298.15 K

	$\Lambda/(s\cdot cm^2\cdot mol^{-1})$					
$10^4\,c$/ mol·dm^{-3}	$x = 0$	$x = 0.0417$	$x = 0.089$	$x = 0.144$	$x = 0.207$	$x = 0.281$
			$CuSO_4$			
1.923	255.40	186.00	124.38	87.22	62.22	39.22
3.704	247.76	176.30	118.38	79.58	54.60	33.62
5.357	241.52	167.00	113.76	74.14	49.86	30.32
6.897	236.28	161.20	110.06	70.10	46.54	28.06
8.334	231.80	155.00	107.00	66.98	44.04	26.40
9.667	227.96	149.72	104.42	64.48	42.08	25.12
10.938	224.54	145.12	102.22	62.40	40.48	24.08
12.121	221.50	142.00	100.28	60.62	39.16	23.22
13.235	218.80	137.80	98.60	59.14	38.04	22.52
14.286	216.42	134.96	97.10	57.84	37.18	21.90
15.278	214.18	133.32	95.76	56.70	36.24	21.36
16.916	212.18	131.84	94.54	55.68	35.50	20.90
17.105	210.34	129.50	93.46	54.78	34.82	20.48
17.948	208.66	128.00	92.46	53.96	34.26	20.12
18.750	207.10	127.00	91.54	53.24	33.73	19.80
			$MnSO_4$			
1.923	254.68	184.56	121.30	87.58	61.70	38.60
3.703	246.90	171.50	112.70	79.16	53.28	33.04
5.357	240.58	162.70	106.50	73.54	48.26	29.72
6.896	235.30	156.00	101.80	69.44	44.80	27.48
8.333	230.78	148.90	97.38	66.28	42.34	25.80
9.677	226.88	144.50	94.32	63.73	40.38	24.54
10.937	223.42	139.70	91.76	61.64	38.62	23.46
12.121	220.38	135.28	89.56	59.88	37.30	22.64
13.235	217.66	131.88	87.66	58.38	36.18	21.92
14.285	215.26	129.10	86.00	57.08	35.22	21.32
15.277	213.00	127.36	84.56	55.92	34.40	20.74
16.216	211.00	125.78	83.32	54.92	33.68	20.30
17.105	209.16	124.34	82.04	54.02	33.02	19.70
17.948	207.50	123.04	80.98	53.20	32.46	19.52
18.750	206.00	121.86	80.02	52.48	31.94	19.30

with the set of equations

$$\Lambda = \alpha[\Lambda_0(1 + \Delta X/X) - \Delta\Lambda_{el}] \qquad (2)$$

$$K_A = (1 - \alpha)/\alpha^2\gamma^2 c \qquad (3)$$

$$-\ln \gamma = \beta\mathbf{k}/2(1 + \mathbf{k}R) \qquad (4)$$

where $\beta = e^2/\epsilon kT$, $\Delta X/X$ is the relaxation field effect, and $\Delta\Lambda_{el}$ is the electrophoretic countercurrent. $\mathbf{k}^{-1}$ is the radius of the ion atmosphere, ϵ is the dielectric constant of the solvent, e is the electron charge, k is the Boltzmann constant, R is the Gurney-sphere diameter, mostly recognized as the ion pair distance, α is the fraction of unpaired solute present, c is the molarity of the solution, γ is the activity coefficient, and β is twice the Bjerrum distance (*21*). The standard deviation

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Table 2. Conductivity Parameters for Metal(II) Sulfates in x Ethanol + 1 − x Water at 298.15 K

x	$\Lambda_0/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$K_A/(\mathrm{mol^{-1}\cdot dm^3})$	$1000_\Lambda/\Lambda_0$
	$CuSO_4$		
0.00	266.16 ± 0.04	188 ± 0.2	0.02
0.0417	214.32 ± 0.02	260 ± 1	0.02
0.089	133.16 ± 0.04	355 ± 1	0.03
0.144	101.84 ± 0.04	575 ± 2	0.03
0.207	78.46 ± 0.06	1318 ± 4	0.03
0.281	53.16 ± 0.04	2951 ± 6	0.03
	$MnSO_4$		
0.00	265.48 ± 0.04	181 ± 0.4	0.04
0.0417	216.40 ± 0.06	247 ± 1	0.03
0.089	140.64 ± 0.08	334 ± 1	0.05
0.144	106.00 ± 0.08	512 ± 2	0.05
0.207	81.52 ± 0.10	1087 ± 6	0.05
0.281	61.34 ± 0.08	2124 ± 8	0.03

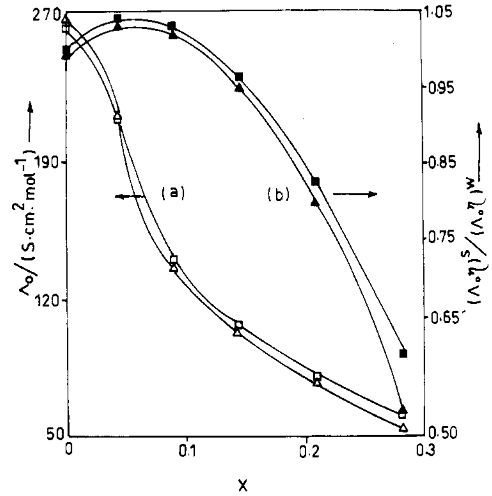

Figure 1. (a) Dependence of limiting molar conductivities for $CuSO_4$ and $MnSO_4$ on x for x ethanol + (1 − x) water at 298.15 K: △, $CuSO_4$; □, $MnSO_4$. (b) Dependence of normalized Walden product values for the salts on x for x ethanol + (1 − x) water at 298.15 K: ▲, $CuSO_4$; ■, $MnSO_4$.

in Λ, *i.e.*, σ_Λ was calculated from

$$\sigma_\Lambda = \{\sum_j [\Lambda_j(\mathrm{calcd}) - \Lambda_j(\mathrm{obsd})]^2\}^{1/2} \qquad (5)$$

An analysis was highly sensitive to the Gurney-cosphere diameter R sometimes taken as the ion pair distance parameter (*18, 20*), the Λ_0 and K_A values are reported at R = 6 Å in Table 2.

The limiting molar conductivities, Λ_0, found for copper sulfate and manganese sulfate in aqueous media are 266.16 and 265.48 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$ at 298.15 K, respectively. The literature values (*1–8, 18, 20*) range from 265.2 to 268.6 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$ for $CuSO_4$ and 267.10 $\mathrm{S\cdot cm^2\cdot mol^{-1}}$ for $MnSO_4$.

The variation of Λ_0 with the composition of ethanol + water for both salts is shown in Figure 1. The figure also includes the dependence of the values of the normalized Walden products $(\Lambda_0\eta)^s/(\Lambda_0\eta)^w$ for these salts on the composition of water + cosolvent. It is found that the Λ_0 values for copper sulfate and manganese sulfate differ from each other in these solvent mixtures. Similar results were found for $MnSO_4$ in other water + cosolvent mixtures (*8*). The Λ_0 decreased with an increase in the ethanol mole fraction. This may be due to the relative increase in the viscosities and the corresponding solvation of the ions. The variation of the normalized Walden product with composition passes through a maximum at about x = 0.09. The plots indicate that initially the ions are solvated with ethanol + water clatherate and then preferential solvation with ethanol occurs with a further increase in the mole fraction of ethanol.

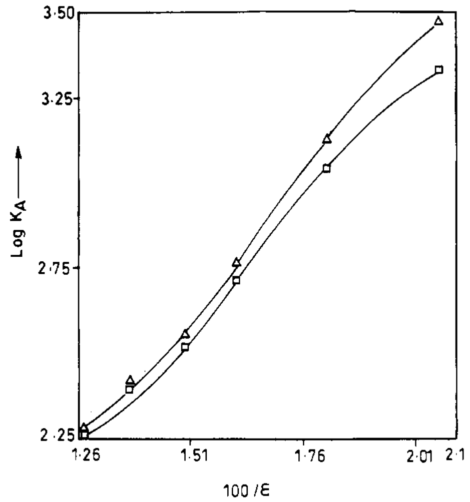

Figure 2. Dependence of log K_A values for the salts on the inverse dielectric constant values ε for ethanol + water at 298.15 K: △, $CuSO_4$; □, $MnSO_4$.

The association constants, K_A, found for these two salts are 188 ± 0.2 and 181 ± 0.4 $\mathrm{dm^3\cdot mol^{-1}}$, respectively, at 298.15 K using R = 6 Å. As reviewed by Wasylkiewicz (*19*), the K_A values found by other researchers are 126–251 $\mathrm{dm^3\cdot mol^{-1}}$ for $CuSO_4$ and 133 to 220 $\mathrm{dm^3\cdot mol^{-1}}$ for $MnSO_4$, respectively, depending on the theory and method. The values of K_A increased as the values of R were varied from 4 to 15 Å. Similar observations were found by other investigators (*18*) in aqueous media. The dependence of K_A on the inverse of the dielectric constant for ethanol + water is shown in Figure 2. The nonlinearity of the plots indicates some specific short-range interactions of the ions with the solvent in addition to simple electrostatic interactions. $CuSO_4$ has been found more associated in ethanol + water compared to $MnSO_4$.

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