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Electrical conductivities of aqueous $ZnSO_4$-H_2SO_4 solutions

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Conductivities of aqueous $ZnSO_4$-H_2SO_4 solutions are reported for a wide range of $ZnSO_4$ and H_2SO_4 concentrations ($ZnSO_4$ concentrations of 0 ~ 1.2 M and H_2SO_4 concentrations of 0 ~ 2 M) at 25° C, 40° C and 60° C. The results indicate that the solution conductivity at a given $ZnSO_4$ concentration is controlled by the H_2SO_4 (H^+) concentration. The variation of the specific conductivity with $ZnSO_4$ concentration is complex, and depends on the H_2SO_4 concentration. At H_2SO_4 concentrations lower than about 0.25 M, the addition of $ZnSO_4$ increases the solution conductivity, likely because the added Zn^{2+} and SO_4^{2-} ions increase the total number of conducting ions. However, at H_2SO_4 concentrations higher than about 0.25 M, the solution conductivity decreases upon the addition of $ZnSO_4$. This behaviour is attributed to decreases in the amount of free water (through solvation effects) upon the addition of $ZnSO_4$, which in turn lowers the Grotthus-type conduction of the H^+ ions. At H_2SO_4 concentrations of about 0.25 M, the addition of $ZnSO_4$ does not appreciably affect the solution conductivity, possibly because the effects of increasing concentrations of Zn^{2+} and SO_4^{2-} ions are balanced by decreases in Grotthus conduction.

Nomenclature

a	ion size parameter (m)
a^*	Bjerrum distance of closest approach (m)
C	stoichiometric concentration ($mol\,m^{-3}$ or $mol\,L^{-1}$)
I	ionic strength ($mol\,L^{-1}$)
k	constant in Kohlrausch's law
M	molar concentration ($mol\,L^{-1}$)
T	absolute temperature (K)
z_i	electrochemical valence of species i ($equiv.\,mol^{-1}$)
z	$(z_+ \lvert z_- \rvert)^{1/2} = 2$ for $ZnSO_4$
z_+	valence of cation in salt ($= +2$ for Zn^{2+})
z_-	valence of anion in salt ($= -2$ for SO_4^{2-})

Greek letters

α	fraction of $ZnSO_4$ dissociated
σ	specific conductivity ($\Omega^{-1} m^{-1}$)
σ_{expt}	measured specific conductivity ($\Omega^{-1} m^{-1}$)
Λ	equivalent conductivity ($\Omega^{-1} m^2 equiv.^{-1}$)
Λ^0	equivalent conductivity at infinite dilution ($\Omega^{-1} m^2 equiv.^{-1}$)
Λ_{calc}	equivalent conductivity calculated using Equation 2 ($\Omega^{-1} m^2 equiv.^{-1}$)
Λ_{expt}	measured equivalent conductivity ($\Omega^{-1} m^2 equiv.^{-1}$)
$\lambda^0(i)$	equivalent conductivity of ion i at infinite dilution ($\Omega^{-1} m^2 equiv.^{-1}$)
χ	reciprocal of radius of ionic cloud (m^{-1})
η	viscosity of solvent (Pa s)
ε	dielectric constant
$\gamma_\pm$	mean molar activity coefficient
ρ	density ($g\,cm^{-3}$)

1. Introduction

The measurement and interpretation of conductance have provided many important insights into the properties of electrolyte solutions. For complex mixed electrolytes such as solutions of $ZnSO_4$ and H_2SO_4, which are commonly used in zinc electrowinning, electrical conductivity plays a particularly important role in economic considerations because of its impact on electrical energy consumption. Therefore, consistent data on electrical conductivities and an understanding of the behaviour of the $ZnSO_4$-H_2SO_4 system are of considerable importance. However, although there have been attempts to predict the behaviour of concentrated $ZnSO_4$-H_2SO_4 solutions [1], to date there has been little published on the electrical conductivity of $ZnSO_4$-H_2SO_4 solutions [2, 3]. Consequently, in the present communication, we report accurate values of the conductivities of $ZnSO_4$-H_2SO_4 solutions measured over a wide range of $ZnSO_4$ and H_2SO_4 concentrations ($ZnSO_4$ concentrations of 0 ~ 1.2 M, and H_2SO_4 concentrations of 0 ~ 2 M).

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2. Experimental details

2.1. *Apparatus*

Electrical conductivities were measured using a Radiometer model CDM83 conductivity meter in combination with a Metrohm model 6.0903 Jones-type measuring cell. The solutions were maintained at the desired temperatures (25° C, 40° C or 60° C) to within ± 0.1° C by immersing the measuring cell in a recirculating constant temperature bath (Julabo, model 5B) containing paraffin oil.

2.2. *Reagents*

All solutions were prepared using deionized water from a Millipore 'Milli-Q' water system (conductivity of $4 \times 10^{-5}\,\Omega^{-1}\,m^{-1}$ after exposure to the atmosphere) and analytical grade reagents: $ZnSO_4 \cdot 7H_2O$, KCl, (both BDH AnalaR), and H_2SO_4 (Baker Analysed). The $ZnSO_4$ and H_2SO_4 concentrations were determined by titration with standardized solutions of ferrocyanide [4] and NaOH, respectively. The method for zinc titrations described in [4] was modified slightly: the ferrocyanide solutions were standardized independently (against solutions of zinc metal (Johnson-Matthey, 99.9999%)), and a blank subtraction was used for the recommended ferricyanide additions. KCl solutions were prepared by weight, using dried KCl.

2.3. *Procedure*

The conductivity meter was calibrated with KCl solutions (see Section 3.1 below). Conductivity readings were recorded every 10–15 min until a stable reading was obtained (most of the readings were stable within 1 h).

3. Results and discussion

3.1. *Cell calibration*

Calibration of the conductivity cell at 25° C with standard KCl solutions (0.009972 M, 0.09969 M and 0.9954 M, having specific conductivities (σ) of $0.1409\,\Omega^{-1}\,m^{-1}$, $1.286\,\Omega^{-1}\,m^{-1}$ and $11.13\,\Omega^{-1}\,m^{-1}$, respectively [5]) gave a cell constant of $5.30\,cm^{-1}$. This cell constant was also used for measurements at 40° C and 60° C, since expansion of the Pyrex cell over 25° C to 60° C was calculated to be negligible. In any event, measured standard values of the conductivities of KCl solutions at 40° C and 60° C are not yet available [6].

3.2. *Conductivities of aqueous $ZnSO_4$ solutions*

The conductivities of aqueous $ZnSO_4$ solutions were measured to verify the efficacy of the measuring system and technique. The conductivities of aqueous $ZnSO_4$ solutions measured over a wide range of concentration (0.0001 ~ 2.6 M) are shown in Fig. 1 and Table 1.

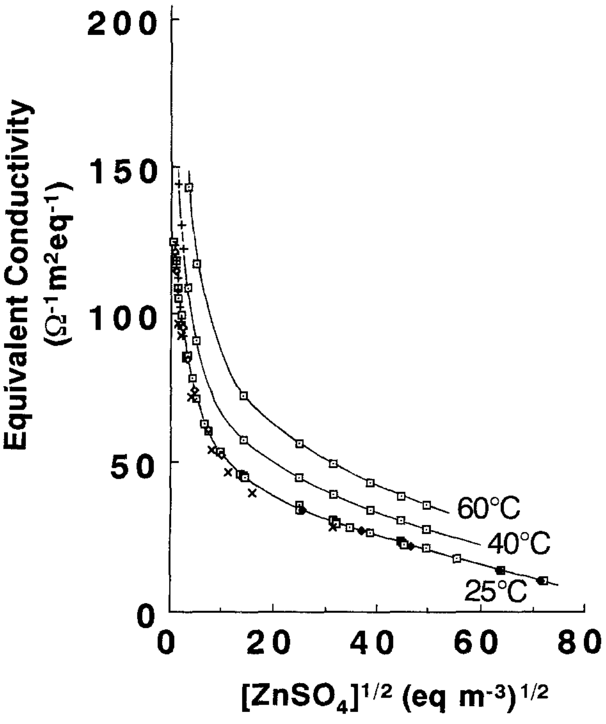

Fig. 1. Measured equivalent conductivities of aqueous $ZnSO_4$ at 25° C, 40° C, and 60° C, and comparison with literature values [7–10]. Key: (⊡) This study, (◆) [7], (+) [8], (◇) [9] and (x) [10].

The excellent agreement between the available literature values [7–10] of the equivalent conductivity, Λ, ($\Lambda = \sigma/(Cz)$, where C is the $ZnSO_4$ concentration, and $z = 2$ for $ZnSO_4$) and the experimental data shown in Fig. 1 confirms the reliability and consistency of the technique and the equipment used.

At low concentrations (less than about 0.001 M), there is a linear relationship between the equivalent conductivity and the square root of the concentration (C), as described by Kohlrausch's Law [11]:

$$\Lambda = \Lambda^0 - k\sqrt{C} \qquad (1)$$

where Λ^0 is the equivalent conductivity at infinite dilution, and k is a constant. A value of $\Lambda^0 = 133.3 \times 10^{-4}\,\Omega^{-1}\,m^2\,equiv.^{-1}$ was obtained by extrapolation of the linear region of the curve for 25° C to infinite dilution. This value is within 0.5% of the literature values of $\Lambda^0 = 132.7 \times 10^{-4} \sim 132.8 \times 10^{-4}\,\Omega^{-1}\,m^2\,equiv.^{-1}$ [9, 11].

A considerable amount of ion association can be expected for a bi-bivalent electrolyte such as $ZnSO_4$ [11]. Such ion pair formation lowers the electrolyte conductivity, since the uncharged ion pairs are non-conducting species. At low concentrations (up to 0.05 M ~ 0.1 M), the degree of ion association of a symmetrical electrolyte such as $ZnSO_4$ can be estimated from measured conductivities, using a modified Onsager equation (see Appendix). Calculated values of α at different concentrations are shown in Table 2 (see Appendix for sample calculation). The value of $\alpha = 0.452$ for 0.103 M $ZnSO_4$ in Table 2 compares well with the value of $\alpha = 0.459$ for 0.102 M, calculated using equilibrium data given in [11]. It can be seen from Table 2 that even at low concentrations, a significant fraction of the $ZnSO_4$ appears to exist as

Table 1. Specific and equivalent conductivities of $ZnSO_4$-H_2O solutions

$[ZnSO_4]$ (*M*)	σ ($\Omega^{-1}m^{-1}$)*			$\Lambda \times 10^4$ ($\Omega^{-1}m^{-2}$equiv.$^{-1}$)†		
	25° C	40° C	60° C	25° C	40° C	60° C
0.000101	0.00256			124.27		
0.000449	0.0106			118.04		
0.000899	0.0196			109.01		
0.00103	0.0217			105.34		
0.00179	0.0356			99.4		
0.00206	0.0396			96.1		
0.00412	0.0706			85.7		
0.00449	0.0772			86.0		
0.00503	0.0866	0.110	0.144	86.1	109	143
0.00898	0.141			78.5		
0.0126	0.180	0.230	0.295	71.4	90.9	117
0.0206	0.259			62.9		
0.0269	0.326			60.6		
0.0449	0.482			53.7		
0.0899	0.829			46.1		
0.0995	0.911	1.15	1.45	45.8	57.8	72.9
0.103	0.921			44.7		
0.308	2.19	2.77	3.49	35.6	45.0	56.7
0.4975	3.06	3.91	4.95	30.8	39.3	49.7
0.512	3.04			29.7		
0.515	3.03			29.4		
0.606	3.44			28.4		
0.746	4.00	5.11	6.50	26.8	34.2	43.5
0.995	4.69	6.07	7.75	23.6	30.5	38.9
1.01	4.65			23.0		
1.03	4.64			22.5		
1.23	5.19	6.76	8.74	21.1	27.5	35.5
1.53	5.43			17.8		
2.04	5.64			13.8		
2.61	5.28			10.1		

* σ = specific conductivity

† Λ = equivalent conductivity = $\sigma/(Cz)$, where C is the $ZnSO_4$ concentration and z = 2 for $ZnSO_4$.

ion pairs, and also that the degree of ion association increases with increasing concentration. Accordingly, a significant fraction of the $ZnSO_4$ in $ZnSO_4$-H_2SO_4 solutions can be expected to form non-conducting $Zn^{2+}SO_4^{2-}$ ion pairs.

3.3. *Conductivities of aqueous H_2SO_4 solutions*

The experimental technique and the accuracy of the apparatus were also checked using the H_2SO_4-H_2O system. The results are shown in Fig. 2 and Table 3. The close agreement between the experimental data and values given in [7] for high H_2SO_4 concentrations is clearly shown in Fig. 2. A value of $\Lambda^0 = 427.6 \times 10^{-4}\Omega^{-1}m^2$equiv.$^{-1}$ was obtained by extrapolation of the data for 25° C, which is within 0.5% of the calculated value of $429.65 \times 10^{-4} \sim 429.8 \times 10^{-4}\Omega^{-1}m^2$ equiv.$^{-1}$, obtained using the values $\lambda^0(H^+) = 349.65 \times 10^{-4} \sim 349.8 \times 10^{-4}\Omega^{-1}m^2$equiv.$^{-1}$ and $\lambda^0(SO_4^{2-})$ =

Table 2. Degree of ion association of $ZnSO_4$ in H_2O at 25° C

$[ZnSO_4]$ (*M*)	α*	% $ZnSO_4$ associated
0.000899	0.887	11.3
0.00898	0.705	29.5
0.0899	0.463	53.7
0.103	0.452	54.8

* See the Appendix for a sample calculation.

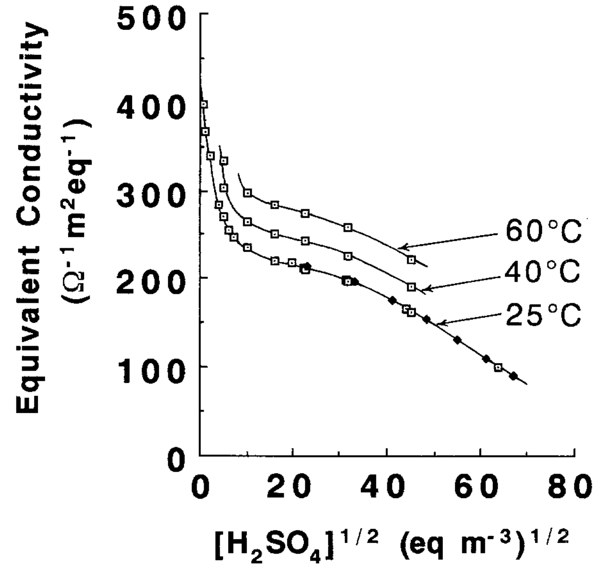

Fig. 2. Measured equivalent conductivities of aqueous H_2SO_4 at 25° C, 40° C, and 60° C, and comparison with literature values [7]. Key: (□) This study and (◆) [7].

Table 3. Specific and equivalent conductivities of H_2SO_4–H_2O solutions

$[H_2SO_4]$ (*M*)	σ ($\Omega^{-1}m^{-1}$)*			$\Lambda \times 10^4$ ($\Omega^{-1}m^{-2}equiv.^{-1}$)†		
	25° C	40° C	60° C	25° C	40° C	60° C
0.000403	0.0320			397.02		
0.00161	0.118			366.46		
0.00403	0.274			340.5		
0.0161	0.915			284		
0.0253	1.37	1.54	1.69	271	304	334
0.0403	2.05			254		
0.0507	2.50			247		
0.101	4.74	5.36	6.01	235	265	298
0.253	11.2	12.7	14.3	221	251	283
0.391	17.0			217		
0.488	20.8			213		
0.507	21.3	24.6	27.8	210	243	274
0.973	38.8			199		
1.01	39.5	45.6	52.4	196	226	259
1.95	65.1			167		
2.02	65.9	77.2	89.8	163	191	222
4.03	81.5			101		

* σ = specific conductivity.
† Λ = equivalent conductivity = $\sigma/(Cz)$, where C is the H_2SO_4 concentration and $z = 2$ for H_2SO_4.

$80.0 \times 10^{-4} \Omega^{-1} m^2 equiv.^{-1}$ for the equivalent conductivities of aqueous H^+ and SO_4^{2-} ions at infinite dilution [9, 11].

The rapid decrease in the equivalent conductivity from 0 ~ 0.1 M (0 ~ 100 mol m^{-3}) H_2SO_4 can be attributed to the presence of an increasing proportion of low mobility bisulfate ions at higher H_2SO_4 concentrations, resulting from incomplete dissociation of the H_2SO_4. At sulfuric acid concentrations greater than about 0.1 M, less than 50% of the acid dissociates completely to H^+ and SO_4^{2-} ions [11].

3.4. *Conductivities of mixed $ZnSO_4$–H_2SO_4–H_2O solutions*

3.4.1. Equilibrium calculations. Equilibrium calculations were made to estimate the concentrations of Zn^{2+}, H^+, SO_4^{2-} and HSO_4^- ions, and the fraction of $ZnSO_4$ dissociated (α) for several of the $ZnSO_4$–H_2SO_4 solutions. The results are shown in Table 4. Such estimation of the speciation in acid-sulfate solutions can provide useful insights into the mechanisms of transport phenomena [12]. The calculation method was the same as that previously described in detail for $CuSO_4$–H_2SO_4 solutions [12], except the equilibrium constant for formation of $Zn^{2+}SO_4^{2-}$ ion pairs was taken as K_1 = antilog (2.38) [1, 13], instead of K_1 = antilog (2.37) for $Cu^{2+}SO_4^{2-}$ ion pairs. The solution densities and the stoichiometric mean activity coefficients for $ZnSO_4$ used in the calculations also are shown in Table 4. The solution densities were measured using relative density bottles (Fisher, 25 mL). The activity coefficients were interpolated from tabulated data for $CuSO_4$–H_2SO_4 solutions [14]. The mean activity coefficients for $ZnSO_4$ and $CuSO_4$ have been shown to be very similar in acid–sulfate solutions [15]. Since the activity coefficient data in [14] are for 0.1 ~ 1.0 M H_2SO_4, we have limited the equilibrium calculations to this range of acid concentrations.

Some interesting behaviour is indicated by the results of the equilibrium calculations. First, a large fraction (40 ~ 70%) of the $ZnSO_4$ added to solutions containing 0.1 ~ 1.0 M H_2SO_4 forms $Zn^{2+}SO_4^{2-}$ ion pairs. Secondly, the H^+ concentration remains approximately constant for a given H_2SO_4 concentration. Furthermore, the fraction of H_2SO_4 completely dissociated remains constant at about 0.6 for H_2SO_4 concentrations of 0.1 ~ 1.0 M, even upon addition of $ZnSO_4$. In this regard, according to [11], the percentage of H_2SO_4 completely dissociated decreases with increasing ionic strength up to an ionic strength of about ~0.6 M (i.e. up to $[H_2SO_4]$ about 0.1 M), but then remains constant at 50 ~ 60% for higher ionic strengths.

3.4.2. Conductivities of aqueous $ZnSO_4$–H_2SO_4 solutions. The measured specific conductivities of aqueous $ZnSO_4$–H_2SO_4 solutions at various concentrations at 25° C, 40° C and 60° C are listed in Table 5. The effects of the $ZnSO_4$ and H_2SO_4 concentrations on the conductivities of $ZnSO_4$–H_2SO_4 solutions at 25° C are summarized in Figs 3 and 4. (A logarithmic scale has been used on the ordinate in Fig. 3 for clarity.)

Figures 3 and 4 show that the specific conductivity increases as the acid concentration is increased at a fixed $ZnSO_4$ concentration. As shown in Fig. 4, the specific conductivity increases linearly with H_2SO_4 concentration at a given $ZnSO_4$ concentration. The equilibrium calculations indicate that the concentration of H^+ remains approximately constant at a given H_2SO_4 concentration, even upon addition of $ZnSO_4$

Table 4. Results of equilibrium calculations for aqueous $ZnSO_4$-H_2SO_4 solutions at 25° C, and values of $\gamma_\pm$ [14] and densitites used in the calculations

$[H_2SO_4]$ (M)	$[ZnSO_4]$ (M)	$[Zn^{2+}]$ (M)	$[H^+]$ (M)	$[SO_4^{2-}]$ (M)	$[HSO_4^-]$ (M)	α	$\gamma_\pm$	ρ $(g\,cm^{-3})$
0.101	0.101	0.057	0.121	0.077	0.081	0.563	0.0950	1.005
	0.308	0.174	0.115	0.188	0.087	0.564	0.0667	1.019
	0.503	0.287	0.116	0.302	0.086	0.570	0.0545	1.083
	0.754	0.415	0.117	0.431	0.085	0.551	0.0468	1.122
	1.01	0.535	0.119	0.553	0.083	0.530	0.0420	1.161
	1.23	0.643	0.120	0.662	0.082	0.523	0.0390	1.199
0.253	0.0995	0.046	0.312	0.105	0.194	0.463	0.0797	1.017
	0.308	0.157	0.301	0.205	0.205	0.509	0.0604	1.029
	0.4975	0.270	0.299	0.316	0.207	0.543	0.0499	1.093
	0.746	0.403	0.301	0.451	0.205	0.540	0.0433	1.132
	0.995	0.526	0.303	0.576	0.203	0.529	0.0392	1.169
	1.23	0.644	0.305	0.696	0.201	0.524	0.0364	1.208
0.507	0.101	0.044	0.635	0.172	0.379	0.434	0.0603	1.031
	0.308	0.148	0.624	0.265	0.390	0.480	0.0502	1.045
	0.503	0.256	0.620	0.369	0.394	0.509	0.0450	1.106
	0.754	0.376	0.620	0.489	0.394	0.499	0.0407	1.147
	1.01	0.488	0.622	0.603	0.392	0.483	0.0377	1.183
	1.23	0.555	0.623	0.671	0.391	0.451	0.0363	1.267
1.01	0.103	0.0275	1.294	0.312	0.725	0.267	0.0524	1.074
	0.207	0.0637	1.290	0.344	0.730	0.308	0.0487	1.097
	0.515	0.197	1.282	0.469	0.738	0.382	0.0411	1.136

(see Table 4). Therefore; the specific conductivity also increases linearly with H^+ concentration, which indicates that the specific conductivity at a given $ZnSO_4$ concentration is controlled by the H^+ concentration.

As seen in Figs 3 and 4, the variation of the specific conductivity with $ZnSO_4$ concentration is complex, and the type of variation depends on the H_2SO_4 (H^+) concentration. Three distinct forms of variation of the specific conductivity with the $ZnSO_4$ concentration are clearly distinguishable (see Figs 3 and 4). At H_2SO_4 concentrations less than about 0.25 M, the solution conductivity at a fixed acid concentration increases as the concentration of $ZnSO_4$ is increased. Conversely, at H_2SO_4 concentrations greater than 0.25 M, the solution conductivity decreases as the concentration of $ZnSO_4$ is increased. At an acid concentration of about 0.25 M, the solution conductivity remains approximately constant over a wide range of $ZnSO_4$ concentrations. As shown in Figs 5 and 6, similar trends are observed at 40° C and 60° C, although as expected, the conductivities increase in magnitude as the temperature is increased.

3.4.2.1. Behaviour at low H_2SO_4 concentrations. At relatively low acid concentrations (less than about 0.25 M), the electrical conductivity increases as the $ZnSO_4$ concentration increases (Figs 3 and 4). According to the equilibrium calculations, the concentrations of H^+ and HSO_4^-, as well as the fraction of $ZnSO_4$ associated, remain approximately constant at a given H_2SO_4 concentration (Table 4). Therefore, at low H_2SO_4 concentrations, for example, 0.1 M, the addition of $ZnSO_4$ increases the total number of conducting ions, and consequently, increases the specific conductivity. The slower rate of increase of the specific conductivity at higher $ZnSO_4$ concentrations may be the result of increasing solution viscosity as well as increasing interference with ionic motion from the larger number of dissolved particles.

3.4.2.2. Behaviour at high H_2SO_4 concentrations. At relatively high acid concentrations (greater than about 0.25 M H_2SO_4), the specific conductivity decreases upon addition of $ZnSO_4$ (Figs 3 and 4). The equilibrium calculations (Table 4) indicate that at a given $ZnSO_4$ concentration, as the H_2SO_4 concentration is increased, the fraction of $ZnSO_4$ dissociated decreases. Thus, as the H_2SO_4 concentration is increased, the H^+ ion concentration increases, while the Zn^{2+} and SO_4^{2-} concentrations decrease, and consequently migration of highly-mobile H^+ ions accounts for an increasing proportion of the solution conductivity at a given $ZnSO_4$ concentration. The high mobility of H^+ ions is due to Grotthus conduction, in which H^+ ions jump from hydronium ions to water molecules, resulting in the migration of H^+ ions [1]. Thus, the transport of H^+ is influenced by the number of free water molecules available for Grotthus conduction. The addition of $ZnSO_4$ lowers the amount of free water, because water of hydration is taken up by the added $ZnSO_4$. (Furthermore, the water of hydration required per mole of $ZnSO_4$ increases with increasing $ZnSO_4$ concentration [16].) The decreases in the amount of free water upon the addition of $ZnSO_4$ result in slowed transport of H^+ ions, which is observed as decreases in the conductivity, as shown by the results for 0.5 ~ 2.0 M H_2SO_4 in Figs 3, 5 and 6.

Water activity has been used by previous workers as a measure of the amount of free water in $ZnSO_4$-H_2SO_4 solutions [1]. Accordingly, to test this

Table 5. *Specific conductivities* of $ZnSO_4$–H_2SO_4 solutions at various temperatures and concentrations*

$[H_2SO_4]$ (*M*)	*0.0253 M*			*0.101 M*			*0.253 M*			*0.507 M*			*1.01 M*			*2.02 M*		
Temp. ⟶ $[ZnSO_4]$ (*M*)	25° C	40° C	60° C	25° C	40° C	60° C	25° C	40° C	60° C	25° C	40° C	60° C	25° C	40° C	60° C	25° C	40° C	60° C
0	1.37	1.54	1.69	4.74	5.36	6.01	11.2	12.7	14.3	21.3	24.6	27.8	39.5	45.6	52.4	65.9	77.2	89.8
0.0129		1.55	1.66	4.67	5.26	5.81	11.1	12.5	14.0		24.4	27.5				65.7	76.9	89.5
0.0258	1.45			4.63						21.3			38.9	44.8	51.2	65.2		
0.0515	1.53			4.59						20.9			38.6	44.6	50.9	64.7		
0.0773				4.57														
0.0995		2.04	2.27				10.5	11.7	12.75									
0.101				4.58	5.06	5.37											74.5	86.4
0.103				4.58									37.8	43.4	49.5			
0.129	1.92			4.62						20.1			37.4	43.0	48.8	62.6		
0.180										19.5								
0.207													35.4	40.6	45.6			
0.258	2.59			4.92						19.0			34.9	40.4	45.2	59.7		
0.308		3.47	4.15	5.08	5.78	6.34	10.1	11.1	11.8		20.8	22.6					68.5	80.1
0.386																56.6		
0.4975		4.54	5.55				10.1	11.2	12.1									
0.503				5.69	6.60	7.50					19.7	21.3					63.6	74.3
0.515	3.69			5.73						17.7			32.3	36.7	40.9	53.8		
0.653																51.5		
0.746		5.70					10.2	11.6	12.9									
0.754				6.38	7.57	8.83					18.9	20.5					58.1	68.15
0.927																		
0.995		6.60	8.33				10.2	11.9	13.6									
1.02	5.17			6.79	8.31	9.99				16.1	18.3	20.3	27.2	31.4	35.0		52.8	62.0
1.23	5.61	7.26	9.24	7.07	8.81	10.80	10.2	12.0	14.1	15.3	17.8	20.0	25.0	29.2	32.9		48.0	56.7
1.31																39.6		

* Specific conductivities in $\Omega^{-1} m^{-1}$.

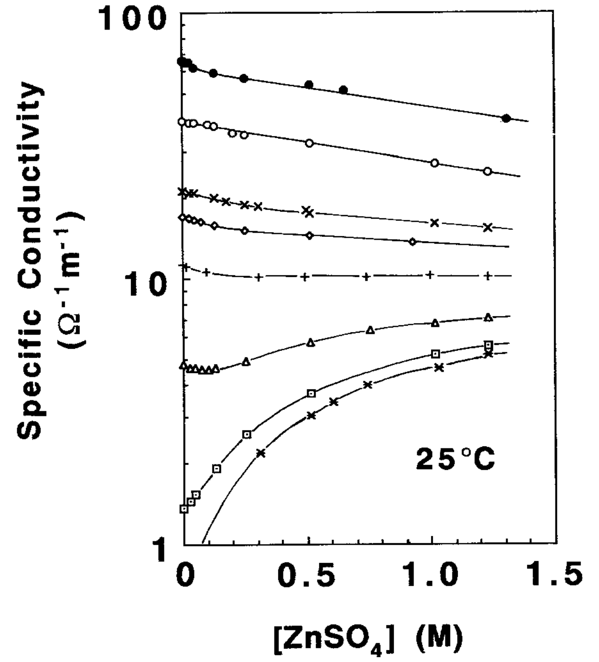

Fig. 3. Variation of the specific conductivity of aqueous $ZnSO_4$–H_2SO_4 solutions with $ZnSO_4$ concentration at different constant H_2SO_4 concentrations at 25° C. [H_2SO_4]: (*) 0, (□) 0.0253, (△) 0.101, (+) 0.253, (◇) 0.398, (x) 0.507, (○) 1.01 and (●) 2.02 M.

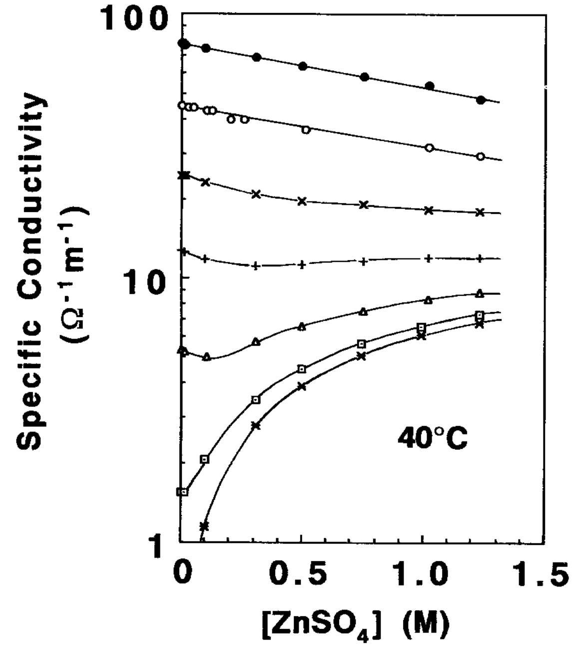

Fig. 5. Variation of the specific conductivity of aqueous $ZnSO_4$–H_2SO_4 solutions with $ZnSO_4$ concentration at different constant H_2SO_4 concentrations at 40° C. [H_2SO_4]: (*) 0, □ 0.0253, (△) 0.101, (+) 0.253, (x) 0.507, (○) 1.01 and (●) 2.02 M.

hypothesis, the measured specific conductivities are plotted in Fig. 7 against the water activities reported in [17]. The same three regions observed when the conductivities are plotted against the $ZnSO_4$ concentrations (Figs 3 and 4) are observed when the conductivities are plotted against the reported water activities (although the plot against water activities is less readily understandable and therefore perhaps less useful). The curves for 0.5 M and 1.0 M H_2SO_4 indicate that, for H_2SO_4 concentrations greater than about 0.5 M, the specific conductivities increase as the water activity increases (although not linearly). However, as can be seen from Fig. 7, the conductivities do not increase significantly with increasing water activity when the H_2SO_4 concentration is 0.25 M; indeed, in 0.1 M H_2SO_4, the conductivities actually decrease with increasing water activities. Thus, factors other than water activity must account for the trends observed at lower acid concentrations, as is discussed in the preceding section.

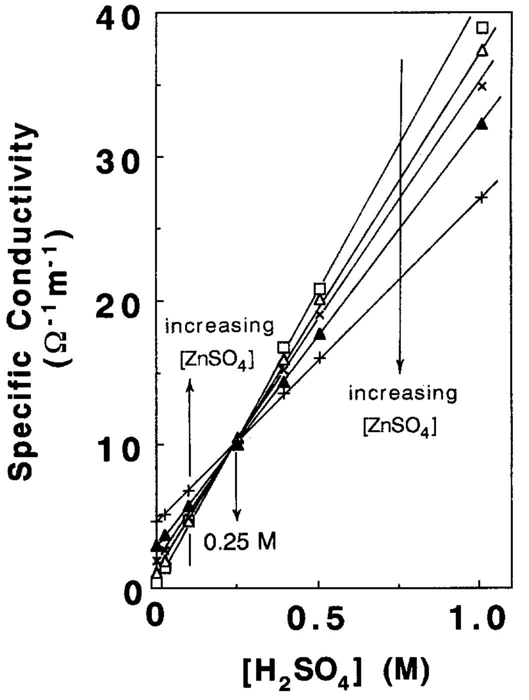

Fig. 4. Variation of the specific conductivity of aqueous $ZnSO_4$–H_2SO_4 solutions with H_2SO_4 concentration at different constant $ZnSO_4$ concentrations at 25° C. [$ZnSO_4$]: (□) 0.0258, (△) 0.129, (x) 0.258, (▲) 0.515 and (+) 1.02 M.

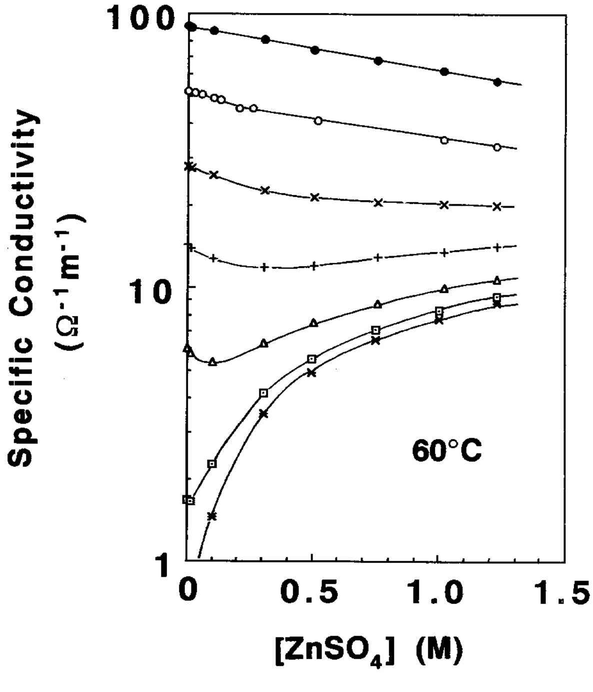

Fig. 6. Variation of the specific conductivity of aqueous $ZnSO_4$–H_2SO_4 solutions with $ZnSO_4$ concentration at different constant H_2SO_4 concentrations at 60° C. [H_2SO_4]: (*) 0, (□) 0.0253, (△) 0.101, (+) 0.253, (x) 0.507, (○) 1.01 and (●) 2.02 M.

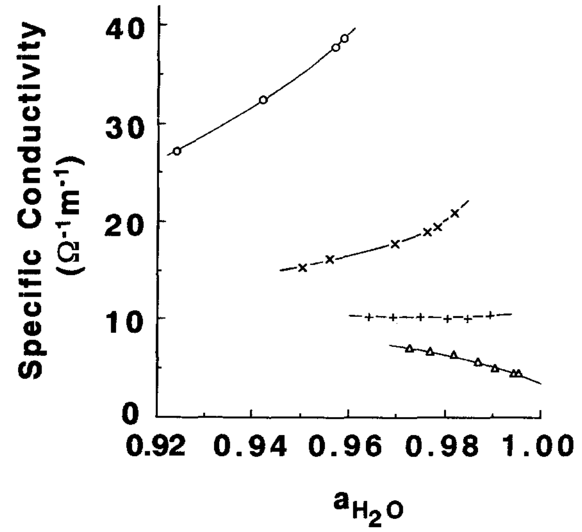

Fig. 7. Variation of the specific conductivity of aqueous $ZnSO_4$–H_2SO_4 solutions with water activity at different constant H_2SO_4 concentrations at 25° C. [H_2SO_4]: (△) 0.10, (+) 0.25, (x) 0.50 and (○) 1.0 M.

3.4.2.3. Behaviour at intermediate H_2SO_4 concentrations. The specific conductivity remains approximately constant upon the addition of $ZnSO_4$ to solutions containing 0.25 M H_2SO_4 (Figs 3 and 4). The H^+ ion concentration in 0.25 M H_2SO_4 at 25° C is about 0.3 M; accordingly, a significant fraction of the solution conductivity can be attributed to Grotthus conduction. Therefore, on the one hand, addition of $ZnSO_4$ lowers the amount of free water, which hinders the mobility of the H^+ ions, and thus tends to lower the specific conductivity. On the other hand, since about half of the added $ZnSO_4$ is dissociated, the presence of increasing concentrations of Zn^{2+} and SO_4^{2-} ions tends to increase the specific conductivity. These two opposing effects may balance one another, resulting in the observed approximately constant specific conductivities in about 0.25 M H_2SO_4.

4. Summary

Conductivities of mixed $ZnSO_4$-H_2SO_4 solutions have been reported for a wide range of $ZnSO_4$ and H_2SO_4 concentrations ($ZnSO_4$ concentrations of 0 ~ 1.2 M and H_2SO_4 concentrations of 0 ~ 2 M) at 25° C, 40° C and 60° C. The linear variation of the specific conductivity with H_2SO_4 concentration at a fixed $ZnSO_4$ concentration indicates that the solution conductivity at a given $ZnSO_4$ concentration is controlled by the H_2SO_4 (H^+) concentration. The variation of the specific conductivity with $ZnSO_4$ concentration is complex. At H_2SO_4 concentrations less than about 0.25 M, the addition of $ZnSO_4$ increases the solution conductivity, likely because the added Zn^{2+} and SO_4^{2-} ions increase the total number of conducting ions. However, at H_2SO_4 concentrations greater than about 0.25 M, the solution conductivity decreases upon the addition of $ZnSO_4$. This behaviour is attributed to decreases in the amount of free water (through solvation effects) upon addition of $ZnSO_4$, which in turn lowers the (Grotthus-type) conductivity of the H^+ ions. At H_2SO_4 concentrations of about 0.25 M, the addition of $ZnSO_4$ does not appreciably affect the solution conductivity, possibly because the effects of increasing concentrations of Zn^{2+} and SO_4^{2-} ions are balanced by the effects of decreases in the amount of free water.

Acknowledgements

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Appendix

Sample calculation of the degree of ion association in 0.103 M $ZnSO_4$

The degree of ion association of a symmetrical electrolyte such as $ZnSO_4$ can be estimated from measured conductivities, using a modified Onsager equation [11].

$$\Lambda_{\text{calc}} = \Lambda^0 - \left(\frac{2.59456 \times 10^4 z^3 \Lambda^0}{(\varepsilon T)^{3/2}(1 + \chi a^*)} + \frac{2.60856 \times 10^{-5} z^2}{\eta(\varepsilon T)^{1/2}(1 + \chi a^*)}\right)\sqrt{\alpha C} \qquad \text{(A-1)}$$

In Equation A-1, α is the degree of dissociation, defined as $\alpha = \Lambda_{\text{expt}}/\Lambda_{\text{calc}}$, where $\Lambda_{\text{expt}} = \sigma_{\text{expt}}/Cz$. The term Λ_{calc} is calculated using Equation A-1, and $\chi a^* = 1.32876 \times 10^5 z^3(\alpha C)^{1/2}/(\varepsilon T)^{3/2}$.

To calculate the degree of ion association in 0.103 M $ZnSO_4$, the values listed below were substituted into Equation A-1 to give

$$\Lambda_{\text{calc}} = 132.8 \times 10^{-4} - \left(\frac{0.01563 \times 10^{-4}}{1 + 3.024\sqrt{\alpha}}\right)\sqrt{\alpha} \qquad \text{(A-2)}$$

The value of α, the fraction of $ZnSO_4$ dissociated, was calculated by iteration using Equation A-2. An initial estimate of α was substituted into Equation A-2 to calculate an initial value of Λ_{calc}. A new value of $\alpha = (\Lambda_{\text{expt}}/\Lambda_{\text{calc}})$ was then substituted into Equation A-2 to determine another value of Λ_{calc}, and hence α. Iteration was continued until consecutive values of α agreed to three significant figures. The resulting value of α for 0.103 M $ZnSO_4$ was 0.452, i.e. 54.8% of the $ZnSO_4$ was associated.

The numerical values substituted into Equation A-1 to give Equation A-2 were as follows:

$\lambda^0_{Zn^{2+}} = 52.8 \times 10^{-4}\,\Omega^{-1}\,m^2\,\text{equiv.}^{-1}$ [11]
$\lambda^0_{SO_4^{2-}} = 80.02 \times 10^{-4}\,\Omega^{-1}\,m^2\,\text{equiv.}^{-1}$ [11]
Therefore
$\Lambda^0 = (52.8 + 80.02) \times 10^{-4}\,\Omega^{-1}\,m^2\,\text{equiv.}^{-1}$
$= 132.82 \times 10^{-4}\,\Omega^{-1}\,m^2\,\text{equiv.}^{-1}$
$\varepsilon_{\text{water}} = 78.303$ [11]
$\eta_{\text{water}} = 0.8903 \times 10^{-3}\,\text{Pa s}$ [11]
$T = 298.15\,K$
$z = (2 \times 2)^{1/2} = 2$

$C = 0.103\,\mathrm{M} = 103\,\mathrm{mol\,m^{-3}}$

$\Lambda_{\mathrm{expt}} = 44.42 \times 10^{-4}\,\Omega^{-1}\,\mathrm{m^2\,equiv.^{-1}}$

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