J. Chem. Eng. Data 1989, 34, 101-102 101

Conductimetric Studies on Aqueous Solutions of Electrolytes. 2. Conductivities of Zinc Sulfate

Victor H. Acevedo, Juana A. de Morán,* Leopoldo A. Sales, and Margarita M. K. de Zamora

Instituto de Química Inorgânica, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumân, Ayacucho 491, 4000 San Miguel de Tucumân, Argentina

The specific conductances and pH values of aqueous solutions of zinc sulfate were measured in a temperature range from 10 to 50 °C. The pH data were used for correcting the equivalent conductances for hydrolysis. The corrected values of specific conductances were analyzed according to the Lee–Wheaton theory, and Λ_0, R, and K_A were evaluated. The obtained values for these parameters were quite satisfactory up to a maximum concentration of 25 × 10^{-4} mol·dm^{-3}, and the agreement with the literature data for 25 °C was acceptable.

Introduction

The measurement of electrolytic conductivities of aqueous solutions of electrolytes provides a valuable method of studying the ionic interaction.

The conductance behavior of 2–2-type electrolytes was studied by several authors (*1–4*). In these cases the detailed interpretation of the conductance data was very difficult due to hydrolysis and ion association effects.

In a previous work the conductance data of $CuSO_4$ in water were reported. The agreement between our data and the literature values (*1*) was quite satisfactory. The equation developed by Lee and Wheaton (*3*) was chosen in order to check if this equation is capable of fitting satisfactorily the results for hydrolyzed salts in water.

This paper deals with a similar electrolyte, zinc sulfate. Precise data up to a maximum concentration of 25 × 10^{-4} mol·dm^{-3} in the temperature range from 10 to 50 °C were obtained, and values for conductance parameters were calculated.

Experimental Section

The techniques used including the preparation of high-purity conductivity water have been described elsewhere (*4*).

Merck reagent grade zinc sulfate heptahydrate was recrystallized twice from anhydrous ethanol and then twice from conductivity water. The salt was dehydrated at 300 °C and weighed as $ZnSO_4$.

Each solution was made up in volumetric material specially calibrated for this purpose, by weight, taking into account the temperature dependence of the concentration. For checking the corresponding concentrations, samples of the solutions were evaporated at 95 °C and the salt was dehydrated at 300 °C in air and weighed as $ZnSO_4$.

For measurements of electrical conductivity, the digital conductimeter Tacussel CD 78 and immersion-type cells with smooth Pt electrodes calibrated (for the different temperatures of the program (*5*)) with KCl solutions were used. Each concentration was measured at four frequencies and the conductivity extrapolated to infinite frequency. Due correction was made for the solvent contribution to the conductance values of all the salt solutions.

For pH measurements, the Orion 701 A digital pH meter with an accuracy of ±0.001 pH units was used. The temperature of the bath was checked against two NPL calibrate thermometers and was held constant to 0.005 °C. The computer analysis of the conductance data was performed in a Texas TI 59 microcomputer.

Table I. Corrected Conductivities of $ZnSO_4$ Solutions (Ω^{-1}•cm•mol^{-1})

t,	10^4c, mol·dm^{-3}							
°C	2.00	3.00	4.50	6.00	8.00	12.5	18.0	24.5
10	84.19	82.26	79.90	78.05	75.86	72.07	68.65	65.48
15	96.55	94.28	91.66	89.40	87.00	82.63	78.75	75.18
20	109.72	107.12	104.11	101.69	98.87	93.96	89.57	85.47
25	122.85	119.96	116.56	113.89	110.70	105.34	100.32	95.83
30	136.76	133.65	129.81	126.73	123.38	117.38	111.89	106.82
35	151.26	147.74	143.68	140.39	136.53	130.08	123.95	118.62
40	166.00	162.14	157.61	154.00	149.87	142.58	136.12	130.07
45	181.41	177.17	172.36	168.22	163.85	155.99	148.91	142.32
50	197.40	192.79	187.60	183.19	178.36	169.75	162.19	155.06

Results

Aqueous solutions of zinc sulfate exhibit acid reaction owing to hydrolysis reaction. Zn^{2+} and SO_4^{2-} participate in protolytic reactions and the different equilibria can be expressed as

$$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+ \tag{1}$$

$$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^- \tag{2}$$

In dilute solutions we may assume as negligible the formation of H_2SO_4 and $Zn(OH)_2$.

The hydrolysis effects were analyzed by means of the pH values of the solutions taking into account the activity coefficients and temperature dependence of equilibrium constants.

The limiting ionic conductances for H^+, HSO_4^-, and the dissociation constant for H_2SO_4 were taken from the literature (*6*), while the values of conductances for $Zn(OH)^+$ and of hydrolysis constants were based on the Owen and Gurry (*2*) data and our data (Sales, L. A.; Morân, J. A.; Acevedo, V., manuscript in preparation).

The corrected conductivities of $ZnSO_4$ solutions are given in Table I. The hydrolysis correction for the lowest concentration is 0.25%.

Values of the molar conductivity Λ_0 are quoted for the molar unit (1/2 $ZnSO_4$) and in international ohms. Concentrations are given in terms of the $ZnSO_4$ molar units.

Discussion

In 1974, Fuoss proposed (*7*) a new model for ions in solutions, based on the concept of the Gurney co-sphere surrounding each ion.

Lee and Wheaton (*3*) derived a new conductance equation based on a model almost identical with the one suggested by Fuoss. This equation has the general form

$$\Lambda = f(\Lambda_0 K_A, R) \tag{3}$$

where Λ_0 = equivalent conductance at infinite dilution, K_A = pairwise ion association constant, and R = distance between

0021-9568/89/1734-0101$01.50/0

Table II. Results of Analysis of Data for $ZnSO_4$ in Water[a]

t, °C	Λ_0, $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$	K_A, $dm^3\cdot mol^{-1}$
10	91.66	228
15	104.97	226
20	119.29	225
25	133.60	224
30	148.75	222
35	164.40	220.5
40	180.60	219
45	197.42	218
50	214.88	217

[a] R = 9.3 Å; $\sigma(\Omega)\%$ = 0.04; c_{max} = 25 × 10^{-4} mol·dm^{-3}.

Table III. Corrected Conductivities (Higher Concentrations at 25 °C)

10^3c, mol·dm^{-3}	3.00	3.50	4.00	4.50	5.00	5.50
Λ, $\Omega^{-1}\cdot cm\cdot mol^{-1}$	92.79	90.26	88.23	86.26	84.54	82.96

the ions at which a stable ion pair either contact or are solvent separated.

Expressions for the special case of a single symmetrical electrolyte are obtained by reduction of the Lee–Wheaton general equation and the simplified form (*8*) is

$$\Lambda = \gamma\Lambda_0\{1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3\} - \frac{\rho\kappa}{1+\kappa R}\{1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \kappa R/12\} \quad (4)$$

where C_1–C_5 = complex terms in (κ,R), γ = fraction of solute present as paired ions, $\rho = |z|eF(3\pi\eta \times 299.79)^{-1}$, and $\beta = z^2e^2(DkT)^{-1}$. All other symbols have their usual meanings.

Here (*7*)

$$K_A = \frac{1-\gamma}{\gamma^2 c f_\pm^{\,2}} \quad (5)$$

The extended Debye–Hückel equation was used for the activity coefficient of dissociated species, and for all nonconducting species, the activity coefficient is assumed to be 1.

Table II shows the parameters obtained when fitting our results with the Lee–Wheaton equation.

For results at low concentrations the equation provides a good fit of data. The standard deviation for data up to a maximum concentration of 25 × 10^{-4} mol·dm^{-3} is $\sigma(\Lambda)\%$ = 0.04.

When all data below a concentration of 50 × 10^{-4} mol·dm^{-3} are analyzed, the $\sigma(\Lambda)\%$ rises to 0.065 (Table III).

In order to compare Owen and Gurry's results with ours, we calculated the conductivity values for the same concentrations. For this purpose we applied the Lee–Wheaton equation using the parameter values determined by us. The data exhibit a reasonable agreement.

Data for similar concentration and temperature region have been published by Katayama (*9*), who applied the revised Fuoss–Onsager theory. However, his paper mentions neither hydrolysis correction nor temperature dependence of the concentration (Table IV).

Thermodynamic Functions. The standard enthalpy of association was determined from the linear plot log K against T^{-1}. The standard free energy change and the entropy of association were calculated by means of the thermodynamic equations. The values are $\Delta G°_{298}$ = −13.41 kJ·mol^{-1}, $\Delta S°_{298}$ = 12.87 J·K^{-1}·mol^{-1}, and $\Delta H°$ = −0.18 kJ·mol^{-1}.

Table IV. Comparison of Results (25 °C)

10^4c,	Λ			Λ	
mol·dm^{-3}	calcd	Owen–Gurry	$c_v\%$[a]	Katayama	$c_v\%$[a]
2.00	122.85			123.50	0.53
3.00	119.96			120.73	0.64
4.00	117.66	117.61	0.04	118.28	0.52
6.25	113.41	113.33	0.07		
9.00	109.36	109.25	0.10		
16.00	101.97	101.86	0.11		
25.00	95.49	95.49	0	95.32	0.18

[a] $c_v\% = (|\Lambda_c - \Lambda_l|/\Lambda_c) \times 100$.

K_A and R Values Obtained. When solvent-separated ion pairs are formed, ion association takes place. The reactions may be summarized as

$$A^+ + B^- \overset{K_R}{\rightleftharpoons} (A^+\cdots B^-) \overset{K_S}{\rightleftharpoons} A^+B^- (\rightleftarrows AB) \quad (6)$$

where $(A^+\cdots B^-)$ = solvent-separated ion pairs (SSIP), A^+B^- = contact pair, and AB = neutral molecule.

The equilibrium constants are

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 = (4\pi NR^3/3.000)\exp(z^2e^2/DkTR) \quad (7)$$

$$K_S = \alpha/(1-\alpha) \quad (8)$$

where K_R = association constant for the formation of SSIP, K_S = association constant for the formation of contact ion pairs, α = fraction of paired ions that are present as nearest-neighbor (contact) pairs, and c = concentration of unpaired ions.

Using the Fuoss nomenclature (*7*), the conductimetric pairing constant is

$$K_A = K_R(1 + K_S) \quad (9)$$

For this system, at 25 °C, the results are the following: K_S = 4.10, K_R = 44.1, K_A = 224, and R = 9.3 Å.

In terms of the model proposed, the R value is very reasonable for a system in which ion–dipole forces may be expected to be strong. It indicates the formation of a stable SSIP.

Acknowledgment

We gratefully acknowledge the assistance of Lore S. de Zuccardi in the preparation of the paper.

Registry No. $ZnSO_4$, 7733-02-0.

Literature Cited

(1) Acevedo, V. H.; A. de Morán, J. B.; Sales, L. A. *Can. J. Chem.* **1983**, *61*(2), 267–268.
(2) Owen, B. B.; Gurry, R. W. *J. Am. Chem. Soc.* **1938**, *60*, 3074.
(3) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, 1128.
(4) Pethybridge, A. D.; Spiers, D. J. *J. Electroanal. Chem.* **1975**, *66*, 231.
(5) Barthel, J.; Feuerlein, F.; Neueder, R.; Watcher, R. *J. Solution Chem.* **1980**, *9*(3), 209.
(6) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1965.
(7) Fuoss, R. M. *J. Phys. Chem.* **1978**, *82*, 2427.
(8) Pethybridge, A. D.; Taba, S. S. *J. Chem. Soc., Faraday Trans. 2* **1980**, 369.
(9) Katayama, S. J. *J. Solution Chem.* **1976**, *5*(4), 241.

Received for review July 25, 1986. Revised May 30, 1988. Accepted October 4, 1988.