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Conductometric study of ion association of divalent symmetric electrolytes: I. $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ in water

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Abstract

Electric conductivities of cobalt, nickel, copper and zinc sulfate solutions in water were measured from 5 to 35 °C (steps of 5 °C) in the concentration range $10^{-4}<c/(\text{mol dm}^{-3})<4\times10^{-3}$. Data analysis, based on the chemical model of electrolyte solutions including short-range interactions, yields the limiting molar conductivity Λ^{∞} and the association constant K_A. The standard Gibbs energy, enthalpy and entropy of the ion-pairing process were calculated from the temperature dependence of the ion-association constants.
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Keywords: Electrolyte conductivity; Electrolyte solutions; Cobalt sulfate; Nickel sulfate; Copper sulfate; Zinc sulfate; Chemical model

1. Introduction

In our previous study [1], aqueous magnesium sulfate solutions in water were investigated. In the present paper, we extended our investigation to 2.2 electrolytes in aqueous solutions. Precise measurements on dilute aqueous cobalt, nickel, copper and zinc sulfate solutions were carried out and treated in the framework of the lcCM model [2].

Divalent metal ions are among the major inorganic species in natural waters and are also of practical importance as they have significant biological functions. Their hydrated cations tend to behave as weak acids. The hydrolysis reaction which changes the environment of the cation may formally be written as

$$C^{2+}+2H_2O \rightleftharpoons COH^{+}+H_3O^{+} \quad (1)$$

The equilibrium constants for the hydrolysis reaction of the divalent metal cations are in the range between 3×10^{-8} for copper cation [3] and 3.8×10^{-12} for magnesium cation [4] at 298.15 K.

Important theoretical progress was made in recent years by the development of chemical models of electrolyte solutions (lcCM, MSA and their extensions), but experimental conductivity studies using modern methods on polyvalent symmetric electrolytes are rather scarce.

It is commonly assumed that solutions of 2.2 electrolytes may contain different types of ion pairs depending on the electrolyte and its concentration. In the concentration range studied here, solvent-separated ion pairs are the distinctly dominant type.

2. Experimental

2.1. Materials

Cobalt sulfate ($CoSO_4\cdot7H_2O$, GR for analysis, Merck), nickel sulfate ($NiSO_4\cdot6H_2O$, GR for analysis, Merck), copper sulfate ($CuSO_4\cdot5H_2O$, Reag. PhEur, Merck) and zinc sulfate ($ZnSO_4\cdot7H_2O$, GR for analysis, Merck) were stored under dry nitrogen and used without further purification.

Demineralized water was distilled in a quartz bi-distillation apparatus (DESTAMAT Bi18E, Heraeus). The final product with specific conductivity of less than 6×10^{-7}

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Ω^{-1} cm^{-1} was distilled into a flask-permitting storage and transfer of the solvent into the measuring cell under a nitrogen atmosphere.

The stock solutions were prepared by adding weighed amounts of water to the weighed amounts of salts. Their concentrations were checked by titration with EDTA (Merck).

2.2. Thermostat

The thermostat used in the experiments of our laboratory has been described previously [1]. It can be set to each temperature of a temperature program with a reproducibility of less than 0.003 K.

Table 1
Equivalent conductivities of $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ in water[a]

$\tilde{m}$ (10^3)	T=278.15	T=283.15	T=288.15	T=293.15	T=298.15	T=303.15	T=308.15
$CoSO_4$, D=0.1590							
0.22001	73.723	84.867	96.782	109.245	122.080	135.415	149.386
0.46111	70.273	80.956	92.149	103.861	116.083	128.626	141.632
0.70703	67.766	78.033	88.771	100.029	111.633	123.703	135.807
0.93856	65.939	75.885	86.340	97.214	108.443	119.866	131.769
1.1744	64.334	74.014	84.186	94.774	105.581	116.855	128.401
1.4078	62.941	72.426	82.324	92.601	103.212	114.185	125.428
1.6993	61.409	70.630	80.265	90.295	100.644	111.297	122.167
1.9875	60.116	69.092	78.522	88.303	98.414	108.773	119.376
2.3530	58.649	67.412	76.581	86.149	95.947	106.046	116.290
2.7029	57.439	66.059	75.017	84.309	93.900	103.729	113.717
3.1092	56.200	64.618	73.370	82.470	91.815	102.163	111.086
3.5193	55.086	63.305	71.860	80.785	89.914	99.231	108.754
$NiSO_4$, D=0.1644							
0.26418	73.036	84.135	95.866	108.156	120.986	134.275	148.014
0.54623	69.449	79.977	91.052	102.639	114.720	127.166	139.720
0.84764	66.585	76.670	87.260	98.331	109.781	121.575	133.744
1.1650	64.268	73.959	84.160	94.771	105.734	117.104	128.705
1.4957	62.305	71.688	81.552	91.787	102.416	113.330	124.526
1.8325	60.633	69.779	79.326	89.266	99.566	110.146	120.940
2.2184	59.007	67.896	77.182	86.830	96.787	107.032	117.486
2.5906	57.621	66.290	75.343	84.744	94.461	104.398	114.572
3.0007	56.334	64.792	73.632	82.792	92.256	101.960	111.815
3.4238	55.170	63.428	72.069	81.028	90.276	99.672	109.154
$CuSO_4$, D=0.1659							
0.14822	76.161	87.842	100.200	112.8794	126.511	140.490	154.991
0.35667	72.510	83.507	95.138	107.118	119.842	132.888	146.150
0.55012	69.941	80.555	91.639	103.274	115.354	127.804	140.649
0.80361	67.385	77.568	88.218	99.366	110.930	122.764	134.914
1.0533	65.385	75.250	85.579	96.298	107.427	118.824	130.489
1.2998	63.731	73.318	83.335	93.751	104.501	115.561	126.758
1.5537	62.248	71.587	81.351	91.477	101.938	112.609	123.487
1.8124	60.944	70.077	79.606	89.484	99.660	110.054	120.582
2.1194	59.573	68.488	77.770	87.367	97.280	107.254	117.581
2.5040	58.083	66.761	75.774	85.117	94.698	104.460	114.328
2.9576	56.573	64.991	73.752	82.776	92.077	101.494	110.990
3.4721	55.083	63.256	71.761	80.512	89.506	98.602	107.781
$ZnSO_4$, D=0.1672							
0.13954	74.949	86.440	98.546	111.310	124.581	138.394	152.186
0.29193	72.371	83.415	95.042	107.267	119.971	132.963	146.511
0.44648	70.368	81.079	92.348	104.157	116.451	129.114	142.218
0.62889	68.437	78.862	89.758	101.183	113.105	125.368	137.765
0.80390	66.943	77.097	87.751	98.888	110.421	122.227	134.122
0.98832	65.528	75.453	85.847	96.715	107.938	119.523	131.425
1.17684	64.260	73.965	84.164	94.790	105.773	117.063	128.615
1.4090	62.928	72.403	82.356	92.705	103.412	114.394	125.636
1.7409	61.213	70.434	80.082	90.116	100.461	111.125	121.989
2.0838	59.728	68.692	78.102	87.863	97.910	108.219	118.745
2.4248	58.425	67.214	76.377	85.889	95.695	105.715	115.870
2.8769	56.925	65.466	74.369	83.614	93.142	102.869	112.785

[a] Units: $\tilde{m}$, mol kg^{-1}; T, K; Λ, S cm^2 mol^{-1}; D, kg^2 dm^{-3}.

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