Electrical Conductivity of Concentrated Aqueous Solutions of Divalent Metal Sulfates

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The electrical conductivities of aqueous solutions of cobalt sulfate, copper sulfate, cadmium sulfate, manganese sulfate, nickel sulfate, and zinc sulfate have been measured as a function of concentration, $m = (0.005$ to $2.5)\ \mathrm{mol\cdot kg^{-1}}$, and temperature, $T = (278.15$ to $308.15)$ K. Densities were measured for all electrolyte solutions at 298.15 K, and the molar conductivities are reported. The conductivity data were analyzed by the empirical Casteel−Amis equation.

Introduction

Divalent metal sulfates are representative divalent symmetrical electrolytes that have been widely investigated in the past few years. Their solutions are appropriate for testing various theories of strong electrolyte behavior and for studying ion association in solution.

Some of the recent studies of ion association of divalent metal sulfates have been limited to dilute aqueous[1,2] or mixed solvent solutions.[3] Electrical conductivity measurements in the concentration range studied there yielded the appropriate overall equilibrium constants of ion association using the low concentration chemical model (lcCM).[4] They are in reasonable agreement with values obtained by dielectric relaxation spectroscopy (DRS) measurements on $MgSO_4$,[5] $CoSO_4$,[6] $NiSO_4$,[6] and CuSO4[7] aqueous solutions. These data clearly demonstrate that, in the investigated aqueous solutions of divalent metal sulfates, three ion-pair types, double solvent-separated, solvent-shared, and contact ion pairs, exist simultaneously in varying ratios at all practicable concentrations. Moreover, DRS also provides valuable information about the possible existence of other higher-order species (triple ions) in solution. Whereas triple ions have been detected in $MgSO_4$,[5] $CoSO_4$,[6] and $NiSO_4$ aqueous solutions,[6] there is no evidence for the formation of triple ions in $CuSO_4$ aqueous solutions.[7] It may therefore be significant that the major difference between these solutions resides in the formation of triple ions, which form even at modest salt concentrations. Although important theoretical progress has been made in recent years, there is no good fundamental theoretical explanation of the behavior of 2,2-electrolyte solutions at high concentrations.

Even reliable conductance data from concentrated solutions of divalent metal sulfates are rather scarce.[8–10] Accordingly, a systematic study is presented in this paper of the electrical conductivities of aqueous solution of $CdSO_4$, $CoSO_4$, $CuSO_4$, $MnSO_4$, $NiSO_4$, and $ZnSO_4$, from moderate to high concentration, $m = (0.005$ to $2.5)\ \mathrm{mol\cdot kg^{-1}}$, over the temperature range $T = (278.15$ to $308.15)$ K. The Casteel−Amis equation[8] was used to exemplify the reproduction of data for technical use.

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Table 1. Coefficients of the Polynomials Obtained by a Least-Squares Method from Measured Densities at 298.15 K

	A / $\mathrm{kg^2\cdot dm^{-3}\cdot mol^{-1}}$	B / $\mathrm{kg^3\cdot dm^{-3}\cdot mol^{-2}}$	C / $\mathrm{kg^4\cdot dm^{-3}\cdot mol^{-3}}$	D / $\mathrm{kg^5\cdot dm^{-3}\cdot mol^{-4}}$
$CdSO_4$	0.2007	0.0262	0.0105	−0.0003
$CoSO_4$	0.1640	−0.0050	0.0243	−0.0064
$CuSO_4$	0.1652	0.0030	0.0211	−0.0073
$MnSO_4$	0.1474	0.0046	0.0088	−0.0016
$NiSO_4$	0.1630	0.0103	0.0079	−0.0013
$ZnSO_4$	0.1700	−0.0084	0.0311	−0.0082

Materials and Methods

Materials. Cadmium sulfate ($CdSO_4\cdot 8/3H_2O$, GR for analysis, Merck), cobalt sulfate ($CoSO_4\cdot 7H_2O$, GR for analysis, Merck), copper sulfate ($CuSO_4\cdot 5H_2O$, GR for analysis, Merck), manganese sulfate ($MnSO_4\cdot H_2O$, spray dried, p. a. Merck), nickel sulfate ($NiSO_4\cdot 6H_2O$, GR for analysis, Merck), and zinc sulfate ($ZnSO_4\cdot 7H_2O$, GR for analysis. Merck) were stored under dry nitrogen and used as received.

Demineralized water was distilled in a quartz bidistillation apparatus (DESTAMAT Bi18E, Heraeus). The final product with specific conductivity of less than $5\cdot 10^{-7}\ \mathrm{S\cdot cm^{-1}}$ was distilled into a flask that enabled storage under a nitrogen atmosphere.

Solutions were prepared by weight at room temperature, using an analytical balance (Sartorius A200S, Göttingen, Germany) with a precision of 0.1 mg. Metal ion concentrations were determined to ± 0.2 % by complexometric titration with EDTA (Merck).

The densities of the solutions at 298.15 K were determined by the method of Kratky et al.[11] using a Paar densitometer (DMA 60, DMA 601 HT). The concentration dependence of the solution density was calculated from the relation

$$\rho = \rho_0 + A\tilde{m} + B\tilde{m}^2 + C\tilde{m}^3 + D\tilde{m}^4 \qquad (1)$$

where $\tilde{m}$ is the molonity of the electrolyte (moles of electrolyte per kilogram of solution). The average absolute deviation between measured and calculated values from this polynomial equation for density at 298.15 K was less than 0.02 %. The densities ρ_0 of pure solvent were taken from the literature[12] and are listed in Table A in the Supporting Information. The coefficients A, B, C, and D obtained for the investigated

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Table 2. Specific Conductivities, κ, of $CdSO_4$, $CoSO_4$, $CuSO_4$, $MnSO_4$, $NiSO_4$, and $ZnSO_4$ in Aqueous Solutions

		T/K						
$\tilde{m}$ / mol·kg^{-1}	ρ(298.15 K) / kg·dm^{-3}	278.15	283.15	288.15	293.15	298.15	303.15	308.15
				κ/S·cm^{-1}				
				$CdSO_4$				
0.00493	0.99806	0.05072	0.05826	0.06577	0.07340	0.08128	0.08925	0.09718
0.01043	0.99918	0.09195	0.10539	0.11880	0.13234	0.14614	0.15998	0.17365
0.02990	1.00314	0.20908	0.23916	0.26872	0.29831	0.32839	0.35831	0.38742
0.05140	1.00753	0.31909	0.36443	0.40933	0.45414	0.49927	0.54391	0.58737
0.10013	1.0175	0.53651	0.61221	0.68685	0.76119	0.83587	0.90960	0.98117
0.20169	1.03874	0.92976	1.05985	1.18803	1.31540	1.44349	1.57009	1.69259
0.40918	1.08421	1.60627	1.82891	2.04939	2.26934	2.49076	2.70987	2.92310
0.60136	1.12951	2.12855	2.42493	2.71761	3.01043	3.30678	3.60101	3.88826
0.82023	1.1851	2.60339	2.96916	3.33131	3.69545	4.06528	4.43489	4.79741
1.00060	1.23443	2.96058	3.37925	3.79118	4.20620	4.62843	5.05358	5.46837
1.20878	1.29586	3.10465	3.56071	4.01361	4.47348	4.94614	5.42304	5.89609
1.37830	1.34990	3.15617	3.63430	4.11176	4.59950	5.10238	5.61215	6.12166
1.48550	1.38575	3.13191	3.61839	4.10649	4.60583	5.12480	5.65213	6.17945
1.60935	1.42978	3.04406	3.53203	4.02498	4.53222	5.06160	5.60142	6.14476
1.79810	1.50075	2.80426	3.28202	3.77071	4.27688	4.80963	5.35704	5.91188
1.93880	1.55684	2.53395	2.99113	3.45812	3.94750	4.46617	5.00353	5.55159
				$CoSO_4$				
0.00551	0.99794	0.05743	0.06599	0.07486	0.08401	0.09334	0.10282	0.11237
0.02535	1.00116	0.19985	0.22930	0.25964	0.29064	0.32196	0.35361	0.38508
0.05135	1.00536	0.33846	0.38817	0.43926	0.49141	0.54391	0.59667	0.64910
0.10139	1.01344	0.57972	0.66452	0.75190	0.84078	0.93031	1.01994	1.10875
0.25225	1.03818	1.18567	1.35907	1.53747	1.71918	1.90234	2.08584	2.26781
0.49488	1.07959	1.96576	2.25438	2.55154	2.85655	3.16352	3.47325	3.77999
0.77057	1.12958	2.63363	3.02518	3.43012	3.84641	4.26959	4.69551	5.12075
0.98266	1.17036	2.98817	3.44021	3.91021	4.39459	4.88849	5.38871	5.88922
1.15112	1.20434	3.16664	3.65552	4.16719	4.69545	5.23458	5.78290	6.33447
1.25691	1.22786	3.22711	3.72802	4.26146	4.80987	5.37181	5.94442	6.51947
1.51929	1.28620	3.18593	3.70856	4.26214	4.83871	5.43299	6.04195	6.65797
1.71911	1.33186	3.03433	3.58548	4.16990	4.76311	5.37382	6.00490	6.64680
				$CuSO_4$				
0.00666	0.99816	0.06658	0.07627	0.08628	0.09649	0.10688	0.11723	0.12752
0.02534	1.00126	0.19599	0.22421	0.25305	0.2822	0.31147	0.34029	0.36859
0.04942	1.00523	0.31936	0.36528	0.412	0.45918	0.5063	0.55273	0.59786
0.09691	1.01309	0.54319	0.62108	0.70039	0.78017	0.85965	0.93772	1.01366
0.25349	1.03939	1.16909	1.33669	1.50758	1.67969	1.85183	2.02082	2.18569
0.3778	1.06088	1.60674	1.83512	2.069	2.30527	2.54124	2.77512	3.00356
0.48810	1.08051	1.94801	2.2289	2.5174	2.80951	3.10251	3.39262	3.67729
0.68062	1.11598	2.49395	2.85367	3.22569	3.60393	3.98522	4.3662	4.74156
0.79347	1.13768	2.75214	3.15377	3.57232	4.00015	4.4331	4.86534	5.29362
0.91975	1.16272	3.00347	3.45278	3.91843	4.39618	4.88061	5.36684	5.85037
1.03712	1.18679	3.22053	3.70303	4.20763	4.7258	5.25388	5.78696	6.31785
1.13837	1.20814	3.33657	3.85155	4.38816	4.94351	5.51046	6.08324	6.65776
1.19810	1.22058	3.40149	3.92907	4.48291	5.05533	5.64149	6.23693	6.83381
				$MnSO_4$				
0.00499	0.99779	0.05236	0.06000	0.06796	0.07611	0.08441	0.09283	0.10127
0.00999	0.99855	0.09222	0.10559	0.11941	0.13354	0.14783	0.16225	0.17659
0.01997	1.00002	0.16031	0.18326	0.20689	0.23091	0.25508	0.27926	0.30317
0.05028	1.0045	0.33305	0.38020	0.42850	0.47724	0.52607	0.57459	0.62218
0.10046	1.01191	0.57539	0.65623	0.73881	0.82192	0.90490	0.98715	1.06749
0.19907	1.02655	1.00980	1.15014	1.29321	1.43702	1.58024	1.72187	1.85991
0.31592	1.04423	1.39247	1.58560	1.78214	1.98028	2.17715	2.37246	2.56305
0.49631	1.07229	1.93302	2.20109	2.47473	2.75094	3.02621	3.29981	3.56722
0.74417	1.11253	2.50265	2.85161	3.20936	3.57116	3.93241	4.29285	4.64611
0.98650	1.15387	2.94844	3.36235	3.78663	4.21694	4.64679	5.07637	5.49735
1.20804	1.19432	3.06780	3.51271	3.97160	4.43973	4.91090	5.38271	5.84947
1.38440	1.22702	3.10369	3.56515	4.04307	4.53241	5.02635	5.52395	6.01635
1.65345	1.28018	2.97707	3.44409	3.93226	4.43451	4.94545	5.46256	5.97759
1.82625	1.31847	2.77937	3.24756	3.72280	4.21098	4.71820	5.23425	5.75034
2.08227	1.37135	2.41317	2.83936	3.29089	3.76172	4.24649	4.74222	5.24275
2.18923	1.39809	2.18669	2.59961	3.02394	3.46536	3.92965	4.40655	4.88859
2.43423	1.45293	1.59800	1.92591	2.28173	2.66092	3.05978	3.47561	3.90332
				$NiSO_4$				
0.00600	0.99802	0.06060	0.06959	0.07895	0.08859	0.09844	0.10847	0.11859
0.02566	1.00123	0.19237	0.22073	0.25010	0.28004	0.31049	0.3412	0.37174
0.04922	1.00509	0.32058	0.36813	0.41676	0.46675	0.5171	0.56788	0.6183
0.12204	1.01709	0.65574	0.75273	0.85223	0.95356	1.05647	1.15907	1.26139
0.25002	1.03854	1.18426	1.35918	1.53827	1.72117	1.90744	2.09251	2.27711
0.36742	1.05867	1.54703	1.77608	2.01217	2.25423	2.49921	2.74632	2.99148
0.49875	1.08177	1.93650	2.22574	2.52106	2.82596	3.13645	3.44689	3.75846
0.67996	1.11480	2.39448	2.75403	3.12481	3.50595	3.89628	4.28656	4.626
0.79690	1.13690	2.63944	3.0382	3.45193	3.87749	4.31308	4.75175	5.19355
1.02243	1.18140	2.99480	3.45597	3.93902	4.43774	4.94935	5.46992	5.99304

Table 2 Continued

$\tilde{m}$ / $\mathrm{mol\cdot kg^{-1}}$	ρ(298.15 K) / $\mathrm{kg\cdot dm^{-3}}$	T/K 278.15	283.15	288.15	293.15	298.15	303.15	308.15
1.15568	1.20894	3.12638	3.61905	4.13230	4.66637	5.21517	5.77151	6.3369
1.39353	1.26050	3.20673	3.7338	4.28784	4.86672	5.46561	6.07843	6.69858
1.60050	1.30800	3.10568	3.63856	4.20240	4.80040	5.41711	6.05528	6.7028
1.78340	1.35192	2.89419	3.42387	3.99009	4.58807	5.2156	5.86395	6.53159
				$ZnSO_4$				
0.00628	0.99809	0.06270	0.07199	0.08164	0.09155	0.1017	0.11192	0.12223
0.02608	1.00141	0.20358	0.23341	0.26413	0.29548	0.32731	0.35903	0.39067
0.05064	1.00555	0.33305	0.38173	0.43179	0.48272	0.5342	0.58547	0.6376
0.10228	1.01414	0.58112	0.66588	0.75295	0.8414	0.93057	1.01935	1.10723
0.20773	1.03196	1.01872	1.16851	1.31995	1.47503	1.63123	1.78664	1.94072
0.47480	1.07896	1.92158	2.20214	2.49175	2.78667	3.08529	3.38386	3.67951
0.74527	1.12979	2.61715	3.00362	3.40435	3.81485	4.23141	4.65057	5.06831
0.95627	1.17199	3.00782	3.46034	3.84753	4.41459	4.90795	5.40674	5.90596
1.19075	1.22175	3.27371	3.78095	4.31113	4.86172	5.4248	5.99613	6.57311
1.29799	1.25072	3.33836	3.86526	4.42032	4.99669	5.58874	6.19422	6.80446
1.48915	1.29366	3.32307	3.86975	4.44884	5.0534	5.67813	6.32038	6.97251
1.62268	1.3267	3.21829	3.76644	4.34889	4.96089	5.59633	6.25217	6.91539
1.82583	1.37789	2.95697	3.49425	4.07217	4.68329	5.32355	5.98961	6.67451

[a] Uncertainities: ρ, ± 0.00007; κ, ± 0.5 %.

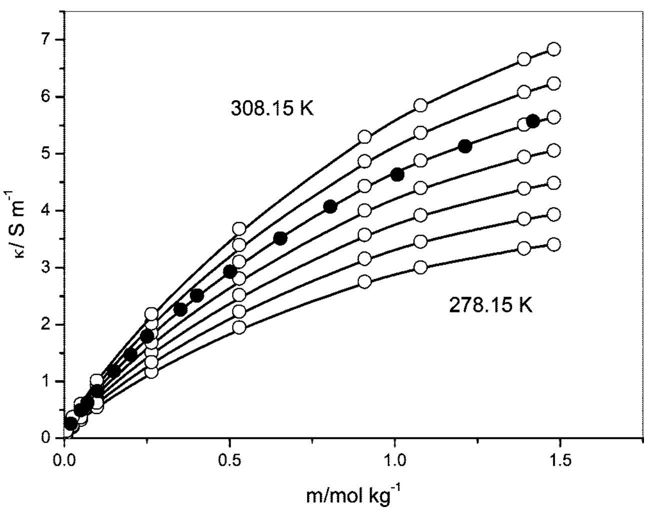

Figure 1. Specific conductivity, κ, of concentrated $CuSO_4$ aqueous solutions at temperatures T = (278.15 to 308.15) K in steps of 5 K as a function of molality, m, yielding Casteel−Amis parameters κ_{max}, μ, a, and b (Table 3). Full lines: eq 3, relative errors between fits and experimental results are less than 0.3 %; ○, measured data, this work; ●, values given in ref 6.

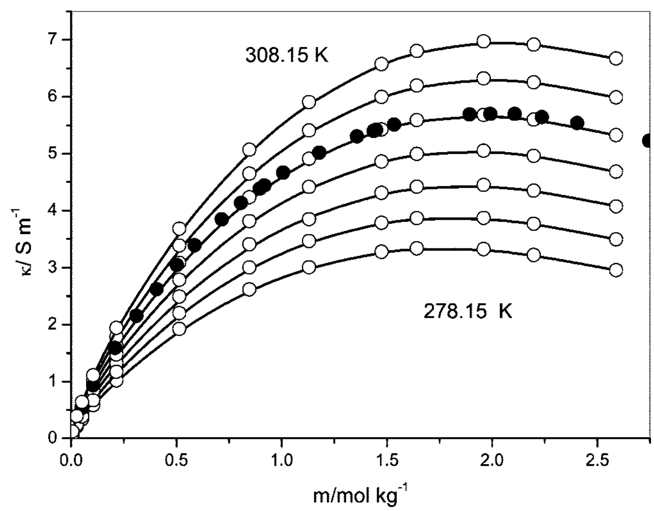

Figure 2. Specific conductivity, κ, of concentrated $ZnSO_4$ aqueous solutions at temperatures T = (278.15 to 308.15) K in steps of 5 K as a function of molality, m, yielding Casteel−Amis parameters κ_{max}, μ, a, and b (Table 3). Full lines: eq 3, relative errors between fits and experimental results are less than 0.2 %; ○, measured data, this work; ●, values given in ref 9.

electrolytes are given in Table 1 and are assumed to be independent of temperature. Molonities $\tilde{m}$ can be transformed to molalities m (moles of electrolyte per kilogram of solvent) and molarities c by

$$m = \frac{\tilde{m}}{1 - \tilde{m}M} \tag{2a}$$

$$c = \rho\tilde{m} \tag{2b}$$

where M is the molar mass of the solute and ρ is the density of the solution (eq 1).

Electrical Conductivity. Conductivity was measured with a set of capillary cells with different cell constants, B', as these are required for concentrated solutions,[13] B' = (~3 to ~85) $\mathrm{cm^{-1}}$. An assembly lid equipped with nine conductivity cells and switch equipment connecting them to the PC-interfaced LCR Meter Agilent 4284 A permits conductivity to be measured at nine different molalities at each temperature.

The cells were calibrated with dilute potassium chloride solutions[14] and immersed in the high-precision thermostat described previously.[15] The oil bath was set to each temperature of a temperature program with a reproducibility within 0.005 K. The temperature was checked with a calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) connected to an HP 3458 A multimeter.

Solutions of different concentrations, known by weight, were transferred under nitrogen into the capillary cells, and measurements were carried out over a temperature cycle beginning and ending at 278.15 K. The cell arrangement permits conductivity to be measured at nine concentrations at each temperature. A home-developed software package was used for temperature control and acquisition of conductance data. The measuring procedure and the extrapolation of the sample conductivity to infinite frequency are as described.[15]

The measured conductivities are listed in Table 2, together with the densities of the solutions at 298.15 K. The molar concentrations c were determined from weights and used to calculate solution densities ρ (eq 2a) and molar conductivities. Values of c(298.15 K) and of molar conductivities are listed in Table B in the Supporting Information. Taking into account the

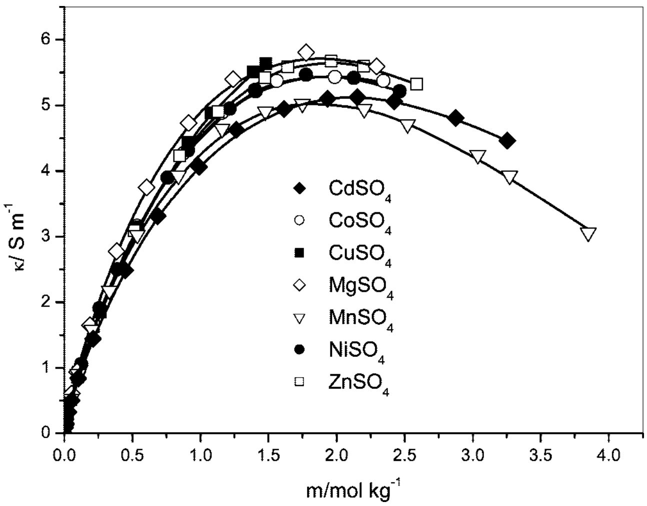

Figure 3. Specific conductivity, κ, of concentrated divalent metal sulfate solutions at 298.15 K as a function of molality, *m,* in water. Full lines: fits according to eq 3, relative errors between fits and experimental results are between 0.1 % and 0.3 %.

sources of error (calibration, titration, measurements, impurities), the specific conductivities are certain within ± 0.5 %.

Results and Discussion

The plots of specific conductivities κ yield functions of molality m with well-defined maxima at all temperatures and electrolytes except for $CuSO_4$(aq), where the solubility determines the accessible concentration range ($m \approx 1.5\ \mathrm{mol \cdot kg^{-1}}$). Examples are given in Figures 1 to 3.

The conductivity data are analyzed using the empirical Casteel−Amis four-parameter equation[8]

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^{a} \exp\left[b(m-\mu)^2 - a\frac{m-\mu}{\mu}\right] \tag{3}$$

known to reproduce well specific conductivity κ as a function of molality m over a wide concentration range around the value of maximum specific conductivity $\kappa_{\max}$ attained at molality μ. The parameters a and b have no physical meaning. The four quantities $\kappa_{\max}$, μ, a, and b are adjusted by a least-squares method. The resulting quantities that reproduce the specific conductivities of the systems investigated at each temperature are listed in Table 3. The temperature shift of the concentration of maximum specific conductivity, $\kappa_{\max}$, is seen to be positive for all the salts investigated.

The existence of maxima in specific conductivity, $\kappa_{\max}$, is the result of competition between the increase of charge carriers and decreasing ionic mobility at increasing electrolyte concentrations. The reasons for this variation of ionic mobility at increasing electrolyte concentration and temperature have been discussed, somewhat controversially, in the literature. Viscosity increase with the electrolyte concentration is the most important but not the only factor. Ion−solvent and ion−ion interactions must also be taken into account.[4,13,16,17]

It was found that, in various solvents and solvent mixtures, $\kappa_{\max}$ and μ are linearly correlated for solutions where ion-pair association is small.[13,17] This indicates an energy barrier to electrolyte conductivity that depends on the solvent properties, particularly viscosity. At concentration μ, the electrolyte exhibits an activation energy of transport, indicating the energy height of the barrier.[17] All the divalent metal sulfates investigated are strongly hydrated salts and exhibit very similar properties in diluted aqueous solution.[2] Figure 3 and Table 3 show that at 298.15 K the maximum of the specific conductivity for all the salts, which is in the range $\kappa_{\max} = (5.5 \pm 0.5)\ \mathrm{S \cdot m^{-1}}$, is situated at molality $\mu = (1.9 \pm 0.2)\ \mathrm{mol \cdot kg^{-1}}$. Due to the low solubility of $CuSO_4$ in water, the maximum here can only be predicted by the Casteel−Amis equation. The most evident difference between the investigated electrolytes is their solubility in water, which could be connected with their ability to form triple ions (or other higher aggregates) in concentrated solutions. As

Table 3. Casteel−Amis Parameters[a]

T / K	$\kappa_{\max}$ / $\mathrm{S \cdot m^{-1}}$	μ / $\mathrm{mol \cdot kg^{-1}}$	a	b
		$CdSO_4$		
278.15	3.164	1.923	0.81056	−0.05112
283.15	3.644	1.969	0.80794	−0.04754
288.15	4.125	2.013	0.80498	−0.04453
293.15	4.619	2.058	0.80249	−0.04190
298.15	5.134	2.106	0.79987	−0.03970
303.15	5.660	2.154	0.79781	−0.03776
308.15	6.189	2.203	0.79537	−0.03626
		$CoSO_4$		
278.15	3.244	1.733	0.80326	−0.07827
283.15	3.764	1.787	0.81031	−0.06505
288.15	4.318	1.841	0.81305	−0.05664
293.15	4.894	1.883	0.81326	−0.05250
298.15	5.488	1.922	0.81263	−0.04986
303.15	6.099	1.963	0.81209	−0.04731
308.15	6.721	2.002	0.81143	−0.04519
		$CuSO_4$		
278.15	3.500	1.834	0.79092	−0.09675
283.15	4.076	1.890	0.79028	−0.08978
288.15	4.686	1.941	0.78960	−0.08504
293.15	5.329	1.992	0.78854	−0.08144
298.15	5.998	2.043	0.78725	−0.07865
303.15	6.694	2.095	0.78623	−0.07596
308.15	7.407	2.147	0.78505	−0.07390
		$MgSO_4$[b]		
278.15	3.409	1.658	0.81862	−0.07170
283.15	3.963	1.700	0.81857	−0.06597
288.15	4.550	1.742	0.81829	−0.06106
293.15	5.165	1.782	0.81817	−0.05697
298.15	5.802	1.823	0.81787	−0.05307
303.15	6.458	1.863	0.81756	−0.04972
308.15	7.130	1.904	0.81718	−0.04667
		$MnSO_4$		
278.15	3.122	1.719	0.80041	−0.06662
283.15	3.588	1.756	0.79582	−0.06315
288.15	4.069	1.789	0.79390	−0.05964
293.15	4.562	1.821	0.79281	−0.05644
298.15	5.064	1.854	0.79058	−0.05391
303.15	5.571	1.886	0.78879	−0.05164
308.15	6.076	1.918	0.78724	−0.04956
		$NiSO_4$		
278.15	3.205	1.733	0.78940	−0.08763
283.15	3.729	1.776	0.79064	−0.08084
288.15	4.283	1.819	0.79151	−0.07529
293.15	4.868	1.862	0.79147	−0.07088
298.15	5.474	1.901	0.79244	−0.06645
303.15	6.101	1.948	0.79211	−0.06326
308.15	6.744	1.991	0.78527	−0.06354
		$ZnSO_4$		
278.15	3.344	1.770	0.79433	−0.08692
283.15	3.881	1.813	0.79412	−0.08094
288.15	4.443	1.871	0.78288	−0.07761
293.15	5.050	1.901	0.79375	−0.07155
298.15	5.670	1.945	0.79331	−0.06772
303.15	6.312	1.990	0.79270	−0.06450
308.15	6.967	2.035	0.79195	−0.06168

[a] Uncertainties: κ, ± 0.01 to 0.02; μ, ± 0.01; a, ± 0.01 to 0.02; b, ± 0.004 to 0.005. [b] Ref 10.

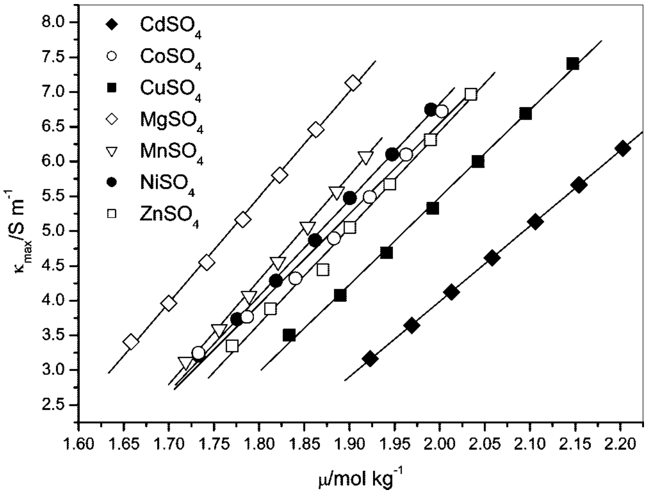

Figure 4. Linear correlation of the maxima of specific conductivities, κ_{max}, and the corresponding molalities, μ, for divalent metal sulfate aqueous solutions in water at temperatures T = (278.15 to 308.15) K. The lines are linear least-squares fits.

mentioned in the Introduction, only in $CuSO_4$ aqueous solutions has no experimental evidence for the formation of triple ions been found.

Although these systems cannot be treated as weakly associating electrolytes, linear relationships for all investigated salts at all temperatures were found (Figure 4), but they do not agree very well. If the dependence of κ_{max} on μ was influenced by the solvent properties only, all the salts should follow the same linear function. Clearly, ion−solvent and ion−ion interactions play a crucial role in concentrated solutions which has not yet been investigated systematically.

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Supporting Information Available:

Tables A and B. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Bešter-Rogač, M.; Babič, V.; Perger, T. M.; Neueder, R.; Barthel, J. Conductometric Study of Ion Association of Divalent Symmetric Electrolytes: I. $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ in Water. *J. Mol. Liq.* **2005**, *118*, 111–118.

(2) Bešter-Rogač, M. Determination of the Limiting Conductances and the Ion-Association Constants of Calcium and Manganese Sulfates in Water from Electrical Conductivity Measurements. *Acta Chim. Slov.* **2008**, *55*, 201–208.

(3) Bešter-Rogač, M.; Hauptman, N.; Barthel, J. Conductometric Study of Ion Association of Divalent Symmetric Electrolytes: II. MgSO4 in Water + 1,4-Dioxane Mixtures. *J. Mol. Liq.* **2007**, *131−132*, 29–35.

(4) Barthel, J.; Krienke, H.; Kunz, W. *Physical Chemisty of Electrolyte Solutions-Modern Aspect;* Steinkoff/Darmstadt, Springer: New York, 1998.

(5) Buchner, R.; Chen, T.; Hefter, G. Complexity in ≫Simple≪ Electrolyte Solutions: Ion Pairing in MgSO4 (aq). *J. Phys. Chem. B* **2004**, *108*, 2365–2375.

(6) Chen, T.; Hefter, G.; Buchner, R. Ion Association and Hydration in Aqueous Solutions of Nickel(II) and Cobalt(II) Sulfate. *J. Solution Chem.* **2005**, *34*, 1045–1066.

(7) Akilan, C.; Hefter, G.; Rohman, N.; Buchner, R. Ion Association and Hydration in Aqueous Solutions of Copper(II) Sulfate from 5 to 65 °C by Dielectric Spectroscopy. *J. Phys. Chem. B* **2006**, *110* (30), 14961–14970.

(8) Casteel, J. F.; Amis, E. A. Specific Conductance of Concentrated Solutions of Magnesium Salts in Water-Ethanol System. *J. Chem. Eng. Data* **1972**, *17*, 55–59.

(9) Price, E. W. Weingärtner, Ion Pairing and Redissociation in Concentrated Aqueous Solution of 2:2 Electrolytes. A Transport Coefficient Study of Aqueous $ZnSO_4$. *J. Phys. Chem.* **1991**, *95*, 8933–8938.

(10) Tomšič, M.; Bešter-Rogač, M.; Jamnik, A.; Nueder, R.; Barthel, J. Conductivity of Magnesium Sulfate in Water from 5 to 35 °C from Infinite Dilution to Saturation. *J. Solution Chem.* **2002**, *31*, 19–31.

(11) Kratky, O.; Leopold, H.; Stabinger, H. Dichtemessung an Flussigkeiten und. Gasen auf 10^{-6} g/cm^3 bei 0,6 cm^3 Präparatvolumen. *Z. Angew. Phys.* **1969**, *27*, 273–277.

(12) Kell, G. S. Precise Representation of Volume Properties of Water at One Atmosphere. *J. Chem. Eng. Data* **1967**, *12*, 66–69.

(13) Barthel, J.; Wachter, R.; Gores, H.-J. Temperature Dependence of Electrolyte Conductance in Non-Aqueous Solutions, In *Modern Aspects of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Eds.; Plenum Press: New York, 1979; pp 1−78..

(14) Barthel, J.; Feuerlein, F.; Neueder, R.; Wachter, R. Calibration of Conductance Cells at Various Temperatures. *J. Solution Chem.* **1980**, *9*, 209–219.

(15) Bešter-Rogač, M.; Habe, D. Modern Advances in Electrical Conductivity Measurements of Solutions. *Acta Chim. Slov.* **2006**, *53*, 391–395.

(16) Barthel, J.; Neueder, R.; Poxleitner, M.; Seitz-Beywl, J.; Werblan, L. Conductivity of Litium Perclorate in Propylene Carbonate+Acetonitrile Mixtures from Infinite Dilution to Saturation at Temperatures from− 35 to 35 °C. *J. Electroanal. Chem.* **1993**, *344*, 249–267.

(17) Barthel, J.; Graml, H.; Neueder, R.; Turq, P.; Bernard, O. Electrolyte Conductivity from Infinite Dilution to Saturation. *Curr. Top. Solution Chem.* **1994**, *1*, 223–239.

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