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Determination of the Limiting Conductances and the Ion-Association Constants of Calcium and Manganese Sulfates in Water from Electrical Conductivity Measurements

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Abstract

Electric conductivities of diluted calcium and manganese sulfate solutions aqueous solutions were measured from 5 to 35 °C (steps of 5 °C) in the concentration range $2 \times 10^{-4} < c/\text{mol dm}^{-3} < 5 \times 10^{-3}$. Evaluation of the limiting molar conductivity Λ^{∞} and the association constant K_A is based on the chemical model of electrolyte solutions, including short-range forces. From the temperature dependence of the limiting molar conductivities Eyring's enthalpy of activation of charge transport was estimated. The standard Gibbs energy, enthalpy and entropy of the ion-pairing process were calculated from the temperature dependence of the ion-association constants. The comparison with some divalent metal sulfates aqueous solutions was made.

Keywords: Divalent metal sulfates, calcium sulfate, manganese sulfate, aqueous solutions, ion association, electric conductivity

1. Introduction

Divalent metal ions are among the major inorganic species in natural waters and are also of considerable practical importance as they have significant biological functions.

Recent investigations on divalent metal sulfates in aqueous solutions[1–4] have demonstrated strong interactions occurring between all particles, ions and solvent molecules. Examination of the results obtained from different techniques[1,2,5–8] shows the interplay of ion association and solvation. The understanding of the nature of the association process is complicated by strong hydration of the free ions. Ultrasonic absorption measurements[9–11] lead to the formulation of a three-stage association process: initially hydrated ions form a double solvent-separated ion pair (2SIP), in which both ion hydration shells remain essentially intact. This step is followed by the formation of a solvent-shared (SIP) and then of a contact (CIP) ion pair. Recently the simultaneous existence of all three ion pair types in $MgSO_4$, $CoSO_4$ and $NiSO_4$ aqueous solutions was demonstrated using dielectric relaxation spectroscopy.[2,4]

In the present work we extended our former investigation on 2,2 electrolytes in dilute aqueous solutions[1,3] to calcium sulfate and manganese sulfate solutions. Many of the physicochemical properties of $CaSO_4$ and $MnSO_4$ are tolerably well known.[12] Nevertheless relatively little reliable information is available on the extent and nature of their association. Some electrical conductance studies of $CaSO_4$[13–15] and $MnSO_4$ (aq)[16–17] solutions have been reported previously. However, the measurements were carried out over limited ranges of temperatures mainly. In this work precise measurements on both systems in water were carried out covering the temperature range from 278.15 K 5 to 308.15 K, and electrolyte concentrations from $\sim 0.2 \times 10^{-3}$ to $\sim 5 \times 10^{-3}$ mol dm^{-3}.

The experimental data were treated in the framework of the low concentration chemical model (lcCM)[18] and the obtained results were compared with the reported values for other divalent metal sulfates aqueous solutions.

2. Experimental

2. 1. Materials

Calcium sulfate ($CaSO_4 \times 2H_2O$, p.a. Merck) and manganese sulfate ($MnSO_4 \times H_2O$) were stored under dry nitrogen and used without preceding purification. Demineralised water was distilled in a quartz bi-distillation apparatus (DESTAMAT Bi18E, Heraeus). The final product with specific conductivity of less than 5×10^{-7} S cm^{-1} was distilled into a flask allowing storage under a nitrogen atmosphere.

Stock solutions of $MnSO_4$ was prepared by adding weighed amount of water to weighed amount of salts and the concentration was checked by titration with EDTA (Merck). Due to the low solubility of $CaSO_4$ in water in this case the stepwise concentration of the solution in the measuring cell was achieved by successive additions of weighed samples of the electrolyte by help of the special designed inlet cap.[19,20]

2. 2. Conductivity Measurement

Conductivity was recorded with a PC-interfaced LCR Meter Agilent 4284 A connected to a three-electrode measuring cell described elsewhere.[19,20] The cell was calibrated with dilute potassium chloride solutions[21] and immersed in the high precision thermostat described previously.[22] The oil bath was set to each temperature of a temperature programme with reproducibility within 0.005 K. The temperature was additionally checked with a calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) connected to an HP 3458 A multimeter.

After measurement of the solvent conductivity at all temperatures of the programme a weighed amount of a stock solution or a solid electrolyte was added and the temperature programme was repeated. A home-developed software package was used for temperature control and acquisition of conductance data. The measuring procedure, including corrections and the extrapolation of the sample conductivity to infinite frequency is described in the literature.[22]

The densities of the solutions were determined by the method of Kratky et al.[23] using of a Paar densimeter (DMA 60, DMA 601 HT) at 25 °C combined with a precision thermostat. From the weights and the corresponding solution densities d the molar concentrations c were determined. As usual, a linear change of density with increasing salt content for dilute solutions was found, $d = d_s + D\tilde{m}$, where d_s is the density of solvent, given in Table 1. $\tilde{m}$ is the molonity of the electrolyte (moles of electrolyte per

Table 1: Densities, viscosities and dielectric constants of pure water and limiting ionic conductances of SO_4^- in water.[a]

T	d_0^b	$\eta \cdot 10^{3c}$	ε^d	$\lambda^\infty(1/2\ SO_4^-)^e$
278.15	0.99997	1.5192	85.897	46.00
283.15	0.99970	1.3069	83.945	53.68
288.15	0.99910	1.1382	82.039	61.81
293.15	0.99821	1.0020	80.176	70.47
298.15	0.99705	0.8903	78.358	80.00
303.15	0.99565	0.7975	76.581	89.47
308.15	0.99404	0.7195	74.846	99.90

[a] Units: T, K; d_0, kg dm^{-3}; η, Pa s; λ^∞, S cm^2 mol^{-1}
[b] Ref.[24]; [c] Ref.[25]; [d] Ref.[26]; [e] Ref.[1]

Table 2: Equivalent conductivities of $CaSO_4$ and $MnSO_4$ in aqueous solutions.[a]

				T			
$\tilde{m} \cdot 10^3$	**278.15**	**283.15**	**288.15**	**293.15**	**298.15**	**303.15**	**308.15**
$CaSO_4$, D = 0.137							
0.67949	71.744	82.427	93.641	105.324	117.364	129.493	142.212
0.93075	69.574	79.962	90.816	102.104	113.634	125.671	137.624
1.22236	67.532	77.576	88.126	99.018	110.145	121.294	127.758
1.71082	64.870			94.967	105.682	116.600	122.254
2.24404	62.505	71.765	84.561	91.400	101.574	111.982	118.409
2.75238	60.690	69.649	81.441	88.615	98.460	108.549	114.386
3.31797	58.840	67.528	78.989	85.892	95.393	104.980	110.921
3.99319	57.225	65.655	74.416	83.324	92.485	101.675	142.212
$MnSO_4$, D = 0.147							
0.29609	71.915	82.889	94.455	106.584	119.152	132.171	145.684
0.61672	68.302	78.637	89.522	100.866	112.611	124.769	137.310
0.90185	66.034		86.426	97.300	108.544	120.142	132.062
1.22932		73.441	83.544	93.984	104.786	115.826	127.197
1.59206	61.929	71.186	80.898	90.956	101.320	111.929	122.796
2.02372	60.024	68.935	78.283	87.949	97.919	108.099	118.508
2.4056	58.573	67.266	76.358	85.774	95.443	105.294	115.356
2.83019	57.175	65.641	74.518	83.647	93.024	102.627	112.351
3.53324	55.271	63.415	71.952	80.700	89.689	98.849	108.163
4.57376	52.935		68.831	77.171	85.698	94.367	103.156

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

kilogram of solution). The density gradient *D*, given in Table 2, was considered to be independent of temperature.

The measured conductivity data of all investigated systems are given in Table 2 as a function of the temperature independent molonities, $\widetilde{m}$, which can be converted to the temperature dependent molarities by use of the relationship

$$c = \widetilde{m}d \tag{1}$$

Taking into account the sources of error (calibration, titration, measurements, impurities) the specific conductivities are accurate to within 0.05% at $MnSO_4$ and 0.2% at $CaSO_4$ solutions.

No hydrolysis correction was made in data analysis.

3. Data Analysis

The analysis of conductivity data in the framework of the low concentration chemical model (lcCM) given in Ref.[18] and the literature quoted there, uses the set of equations

$$\frac{\Lambda}{\alpha} = \Lambda^{\infty} - S\sqrt{\alpha c} + E\alpha c\, ln(\alpha c) + J_1 \alpha c + J_2 (\alpha c)^{\frac{3}{2}} \tag{2}$$

$$K_{\mathrm{A}} = \frac{1-\alpha}{c\alpha^2 y'^2_{\pm}}; \quad y'_{\pm} = exp\left(-\frac{\kappa q}{1+\kappa R}\right);$$

$$\kappa^2 = 16\pi N_A q\alpha c; \qquad q = \frac{e_o^2}{8\pi\varepsilon\varepsilon_o kT} \tag{3a–d}$$

$$K_{\mathrm{A}} = 4\pi N_A \int_a^R r^2 \, exp\left[\frac{2q}{r} - \frac{W^*}{kT}\right] dr \tag{4}$$

where Λ and Λ^{∞} are the molar conductivities at molarity *c* and infinite dilution, $(1-\alpha)$ is the fraction of oppositely charged ions acting as ion pairs, and K_A is the equilibrium constant of the lcCM with upper association limit *R*; $y^{`}_{\pm}$ is the corresponding activity coefficient of the free ions, $(y^{`}_{\pm})^2 = y^{`}_{+}\, y^{`}_{-}$, κ is the Debye parameter, *e* is the proton charge, ε is the relative permittivity of the solvent, ε_o is the permittivity of a vacuum and *T* the absolute temperature. The other symbols have their usual meaning. W^* is a step function for the potential of mean force between cation and anion due to non-coulombic interactions in the association process, see section 4.2.

The coefficients of Eq. (2) are explained in Ref.[18]. The parameters *S* and *E,* which do not depend on the distance parameter *R*, are estimated with the help of the solvent parameters. The coefficients J_1 and J_2 additionally depend on the distance parameter *R* representing the distance up to which oppositely charged ions are counted as non-conducting ion pairs, and hence is the upper limit of ion-pair association represented by the upper limit of the association constant, $K_{A,}$ and the distance parameter of the mean activity coefficient, $y^{`}_{\pm}$ (Eqs. 3 and 4).

Analysis of the conductivity data was carried out by setting the coefficients *S*, *E* and J_1 of Eq. (2) to their calculated values.[18] Then three-parameter fits were used to obtain the limiting values of molar conductivity Λ^{∞}, the association K_A and the coefficient J_2 by non-linear least squares iterations. The input data for the calculation of the coefficients $S, E, J_1, J_2, y^{`}_{\pm}$ are the solvent properties $d(T)$, $\varepsilon(T)$, $\eta(T)$ given in Table 1 and the distance parameter *R*.

The lower limit a of the association integral is the distance of closest approach of cation and anion (contact distance)

$$a = a_+ + a_- \tag{5}$$

calculated from the ionic radii of metal ions (a_+ = 0.106 and 0.091 nm for $Ca^{2'}$ and Mn^{2+}, respectively) and SO_4^{2-} (a_- = 0.258 nm),[18] giving the contact distance a = 0.364 and 0.349 nm for $CaSO_4$ and $MnSO_4$, respectively.

From extended investigations on electrolyte solutions in amphiprotic hydroxylic solvents (water, alcohols) it is known that the upper limit of association is given by an expression of the type

$$R = a + n \times s \tag{6}$$

where s is the length of an oriented solvent molecule, *n* is an integer, $n = 0, 1, 2, \ldots$ Here, s is the length of an OH-group, d_{OH}, and $s = d_{OH} = 0.28$ nm.

4. Results and Discussion

4. 1. lcCM Calculations

Figures 1 and 2 show the experimental data and the results of the lcCM calculations executed by the use of Eqs. 2–6 under the assumption *n* = 2 for Eq. 6 encompassing

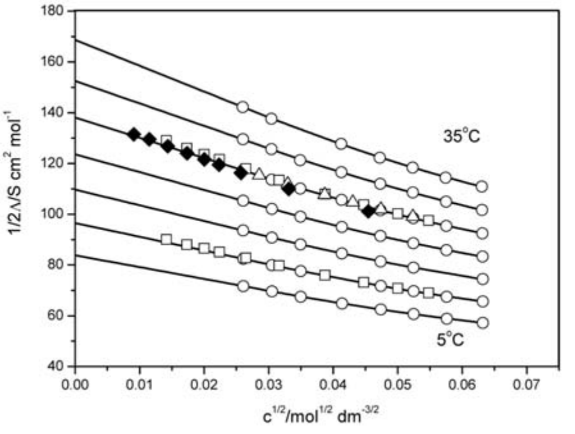

Figure 1:. Equivalent conductivities of aqueous $CaSO_4$ solutions from 5 to 35 °C (steps of 5 °C). (O) this work; (◆) Ref.[13]; (△) Ref.[14]; (☐) Ref.[15]; full line: lcCM calculations.

three types of ion pairs: contact ion pairs, solvents-shared and solvent-separated ion pairs.

The limiting conductivities, Λ^∞, and association constants, K_A, resulting from the data analysis based on the lcCM model are given in Table 3. It shows the comparison of the calculated lcCM data for the cases I (n = 1 for CIP and SIP ion pairs) and II (n = 2 for all investigated ion pairs, CIP, SIP and 2SIP). The limiting conductivities do not differ significantly, as can be expected. $R(J_2)$ calculated from J_2 which is obtained by the data analysis is not necessarily found identical to R which is the input-parameter, $R = a + ns$, chosen for the calculation of J_1 and $y_\pm$, but it may be used as a compatibility control.[18] Here $R(J_2)$ and R are in reasonable agreement for the case I and for the case II as well.

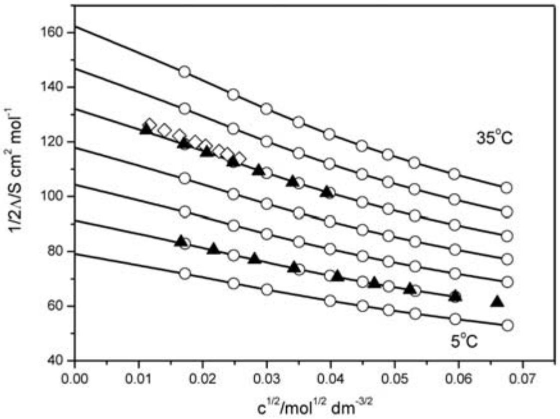

Figure 2: Equivalent conductivities of aqueous $MnSO_4$ solutions from 5 to 35 °C (steps of 5 °C). (O) this work; (◇) Ref.[16]; (▲) Ref.[17]; full line: lcCM calculations.

The conductance data at 298.15 K from the literature and from this work are compared in Table 4. The table compiles data resulting from our redetermination of the authors' original $\Lambda(c)$ data with the help of lcCM calculations. After reevaluation according to the lcCM the earlier measurements are in good agreement with our results.

Calorimetric measurements on the heat of dilution[27] of aqueous solutions at 298.15 K and their data evaluation with the lcCM (n = 2) yield K_A values of 192 (183) and 194 (191) for $CaSO_4$ and $MnSO_4$, respectively, and are in good agreement with the values obtained by our conductivity measurements, given in parenthesis.

Combining the limiting conductivities Λ^∞ of Table 3 and known limiting values of $\lambda^\infty_{SO_4^{2-}}(T)$

$$\lambda^\infty_{M^{2+}}(T) = \Lambda^\infty(T) - \lambda^\infty_{SO_4^{2-}}(T) \qquad (7)$$

Table 4: Comparison of the results at 298.15 K with literature data.[a]

	$1/2\Lambda^\infty$	K_A
$CaSO_4$	138.09 ± 0.28^b	183.0 ± 5.5^b
	138.4 ± 0.2^c	270.5 ± 0.3^c
	136.4 ± 0.3^d	273 ± 9^d
	136.4 ± 0.1^e	239 ± 3^e
$MnSO_4$	132.05 ± 0.07^b	190.6 ± 1.6^b
	132.3 ± 0.1^f	291 ± 4^f
	132.5 ± 0.2^f	276 ± 5^f

Values are redeterminated from the reported data by lcCM (n = 2).
[a]Units: Λ^∞, S cm^2 mol^{-1}; K_A, dm^3 mol^{-1}.
[b]This work, [c]Ref.[15], [d]Ref.[13], [e]Ref.[14], [f]Ref.[17], [g]Ref.[16]

Table 3: Limiting equivalent conductivities, $1/2\Lambda^\infty$, association constants, K_A, and $R(J_2)$ parameter of $CaSO_4$ and $MnSO_4$ solutions in water.[a]

T	$1/2\Lambda^\infty$	K_A I : n = 1	$R(J_2)$	$1/2\Lambda^\infty$	K_A II : n = 2	$R(J_2)$
			$CaSO_4$			
	R = 0.644			R = 0.924		
278.15	83.62±0.12	140.2±5.7	0.672	83.87±0.18	173.5±6.0	0.968
283.15	96.25±0.21	142.2±6.1	0.672	96.55±0.22	176.4±6.5	0.967
288.15	109.42±0.18	141.1±4.5	0.708	109.75±0.0.5	175.4±1.4	0.991
293.15	123.26±0.15	142.82±3.2	0.739	123.65±0.15	177.6±3.3	1.025
298.15	137.65±0.28	147.5±5.5	0.743	138.09±0.28	183.0±5.5	1.029
303.15	152.20±0.71	144.60±12.5	0.797	152.45±0.72	180.4±12.9	1.075
308.15	168.09±2.21	168.9±36.4	0.701	168.68±2.27	206.8±38.4	0.997
			$MnSO_4$			
	R = 0.629			R = 0.909		
278.15	78.95±0.05	129.3 ± 1.7	0.674	79.11±0.03	160.8 ± 1.3	0.979
283.15	91.20±0.05	137.9±1.9	0.631	91.34±0.04	168.1±1.5	0.967
288.15	104.04±0.07	141.0±1.8	0.664	104.25±0.05	173.5±1.4	0.975
293.15	117.63±0.08	149.2±1.9	0.658	117.88±0.06	182.4±1.5	0.972
298.15	131.76±0.09	156.7±2.1	0.606	132.05±0.07	190.6±1.6	0.975
303.15	146.53±0.09	166.8±1.9	0.654	146.85±0.06	201.5±1.3	0.972
308.15	161.96±0.10	178.7±1.9	0.641	162.32±0.07	214.2±1,3	0.969

[a] Units: T, K; Λ^∞, S cm^2 mol^{-1}; K_A, dm^3 mol^{-1}; R, nm.

yields the limiting cation conductivities $\lambda^{\infty}_{\mathrm{M}^{2+}}$ and their temperature dependence (Table 5)

Table 5: Single ion conductivities.[a]

T	$\lambda^{\infty}(1/2\ \mathrm{Ca}^{2+})$	$\lambda^{\infty}(1/2\ \mathrm{Mn}^{2+})$
278.15	37.87	33.11
283.15	42.87	37.66
288.15	47.94	42.44
293.15	53.18	47.41
298.15	58.09	52.05
303.15	62.98	57.38
308.15	68.78	62.42

[a] Units: T, K; λ^{∞}, S cm^2 mol^{-1}.

The temperature dependence of limiting conductivity yields Eyring's enthalpy of activation of charge transport[28]

$$ln\,\lambda^{\infty} + \frac{2}{3} ln\,d_s = -\frac{\Delta H^{\#}}{RT} + B\,, \tag{8}$$

where d_s is the density of the solvent and B is a constant. The obtained values are $\Delta H^{\#} = 13.94$ and 14.94 kJ/mol for Ca^{2+} and Mn^{2+} ion, respectively. It could be assumed that for the jump of the Ca^{2+} in a prepared vacancy in the water-or to produce such a vacancy-less energy is required than for Mn^{2+}.

4. 2. Thermodynamics of the Ion-Pair Process

The association constant $K_A(T)$ is linked to the Gibbs' energy of ion pair formation, $\Delta G_A^0(T)$, *by*

$$\Delta G_A^0(T) = -RT\ ln\ K_A(T). \tag{9}$$

$\Delta G_A^0(T)$ is represented for the measured temperature-dependent association constants of Table 3 with the help of a polynomial

$$\Delta G_A{}^0(T) = A_0 + A_1\,(298.15\text{-}T) + \\ + A_2\,(298.15\text{-}T)^2. \tag{10}$$

Enthalpy and entropy of association here are obtained as follows

$$\Delta S_A^0 = -\left(\frac{\partial \Delta G_A^0}{\partial T}\right)_p = A_1 + 2A_2(298.15 - T) \tag{11}$$

$$\Delta H_A{}^0 = \Delta G_A{}^0 + T\,\Delta S_A{}^0 = A_0 + \\ + 298.15\,A_1 + A_2\,(298.15^2\text{-}T^2) \tag{12}$$

Table 6 compiles the coefficient of the polynomial, Eq. (10). The values of ΔG_A^0 and ΔS_A^0 at 298.15 K are $\Delta G_\mathrm{A}^0 = A_0$ and $\Delta S_\mathrm{A}^0 = A_1$. The comparison of $\Delta H_\mathrm{A}{}^0$ at 298.15 K with the values obtained by calorimetric measurements is also presented.

Figure 3 shows the Gibbs energies ΔG_A^0, enthalpies ΔH_A^0 and entropies ΔS_A^0 of ion-pair formation in $\mathrm{CaSO_4}$ and $\mathrm{MnSO_4}$ aqueous solutions.

The enthalpies of ion-pair formation show reasonable agreement with the values from the calorimetric measurements. The entropies are in the range between 60 and 70 J mol^{-1} K^{-1} as reported for other divalent sulfate aqueous solutions and increase at increasing temperature (Figure 3) suggesting that ion pair formation in the investigated systems is an entropy driven process.

According to the Eq. (4) the Gibbs' energy of ion-pair formation, ΔG_A^0, can be split into two terms

$$\Delta G_A^0 = \Delta G_A{}^{coul} + \Delta G_A^*, \tag{13}$$

where $\Delta G_A^* = N_A W^*$ and ΔG_A^{coul} is obtained from the "coulombic" part of the association constant K_A in Eq. (4)

$$\Delta G_A{}^{coul} = -RT\ ln\ K_A{}^{coul} \tag{14}$$

$$K_A^{coul} = 4\pi N_A \int_a^R r^2\, exp\left[\frac{2q}{r}\right] dr\,. \tag{15}$$

A polynomial of type of Eq. (9)

$$\Delta G_A{}^*(T) = B_0 + B_1\,(298.15\text{-}T) + \\ + B_2\,(298.15\text{-}T)^2 \tag{16}$$

is used for evaluation of the ΔG_A^*, $\Delta H_A{}^*$ and $\Delta S_A{}^*$ of the ion-pair formation presented in Table 7, together with the coefficients B_0, B_1 and B_2 of ΔG_A^* polynomials. It is evident that ΔG_A^* is small in comparison to that of total value of ΔG_A, indicating a preference of strong electrostatically bound ion pairs.

Table 6: Coefficients of polynomials $\Delta G_A^0(T) = A_0 + A_1\,(298.15\text{-}T) + A_2\,(298.15\text{-}T)^2$ and ΔH_A^0 (298.15 K) for $\mathrm{CaSO_4}$ and $\mathrm{MnSO_4}$ in water.[a]

	$A_0 = \Delta G_A^0$ (298.15 K)	$A_1 = \Delta S_A^0$ (298.15K)	A_2	ΔH_A^0 (298.15 K)	
$\mathrm{CaSO_4}$	–12 897	61.48	–0.736	5420	6670[b]
$\mathrm{MnSO_4}$	–13 022	69.38	–0.304	7670	7770[b]

[a] Units: A_0, J mol^{-1}; A_1, J mol^{-1} K^{-1}; A_2, J mol^{-1} K^{-2}; ΔH_A^0, J mol^{-1} [b] Ref.[27] from calorimetry

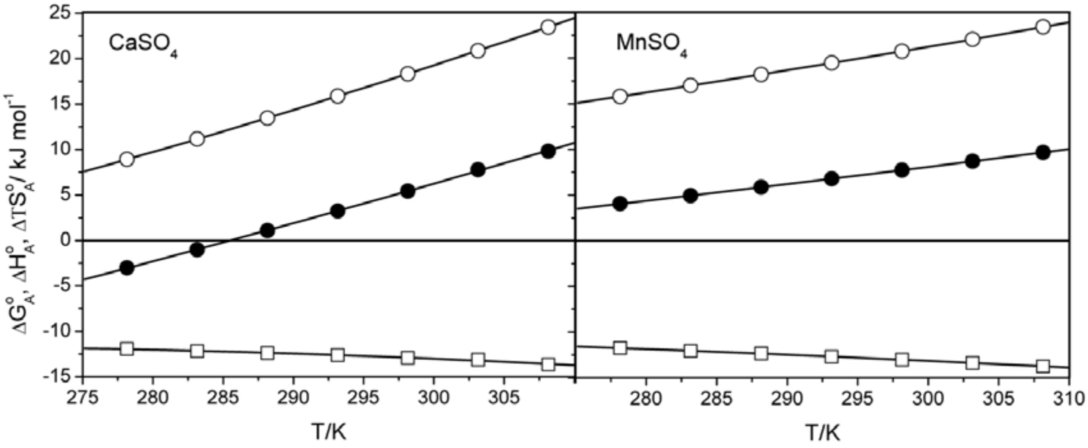

Figure 3: Temperature dependence of thermodynamic functions of association of $CaSO_4$ and $MnSO_4$. (□) ΔG_A^0; (●) ΔH_A^0; (○) $T\Delta S_A^0$.

Table 7: Coefficients of polynomials $\Delta G_A^*(T) = B_0 + B_1\,(298.15\text{-}T) + B_2\,(298.15\text{-}T)^2$ and ΔH_A^* (298.15 K) for $CaSO_4$ and $MnSO_4$ in water.[a]

	$B_0 = \Delta G_A^*$ (298.15 K)	$B_1 = \Delta S_A^*$ (298.15 K)	B_2	ΔH_A^* (298.15 K)
$CaSO_4$	1042	–17.5	0.155	–4232
$MnSO_4$	1465	1.0	–0.140	1784

[a]Units: B_0, J mol^{-1}; B_1, J mol^{-1} K^{-1}; B_2, J mol^{-1} K^{-2}; ΔH_A^* J mol^{-1}

5. Comparison of Some Divalent Metal Sulfates

In some ways this work means a conclusion of our investigations of divalent metal sulfates dilute aqueous solutions. Thus it is reasonable to make a summary and to present a comparison between studied systems as it is made in Table 8.

The most remarkable feature of the present results is the surprising uniformity of the properties of the aqueous solutions of divalent metal sulfates. It can in large part be ascribed to the strong hydration of the ions (and ion pairs) found in these solutions, which tends to attenuate the effects of differences in ion size and electronic configuration.

The hydrated radius is much larger than similar ions and the large solvation shell around the ion also causes its low mobility and low limiting conductivities λ^∞ in solution.

Only $CaSO_4$ and $CuSO_4$ exhibit slightly higher values of λ^∞. Calcium, however, belongs to a group of ions with much weaker hydrogen bonding.[30,31] Recent study of the solvation structures of Mg^{2+} and Ca^{2+} ions in water by applying a Car-Parinello-based constrained molecular dynamics method suggests that the hydration structure of Ca^{2+} is shighly variable.[32] Therefore the higher value of λ^∞ (1/2 Ca^{2+}) can be explained by the assumption that the binding of water molecules in the hydrate shell of Ca^{2+} ion weaker than at other divalent metal ions and thus the motion of Ca^{2+} ions in aqueous solutions is slightly less hindered.

Table 8. Comparison of ionic radii, a_+, ionic limiting conductivities, λ^∞ (1/2 M^{2+}), constants, K_A, entropies, ΔS_A^0, and enthalpies, ΔH_A^0, of ion pair formation, and Eyring's enthalpy of activation of charge transport, $\Delta H^\#$, for divalent sulfates in aqueous solutions.[a]

	a_+^b	λ^∞(1/2 M^{2+})	K_A	ΔS_A^0	ΔH_A^0	$\Delta H^\#$
$CaSO_4$	0.106	58.09	183	61.5	5.42	13.94
$CdSO_4$[c]	0.103	54.06	245	72.0	7.87	14.77
$CoSO_4$[d]	0.082	53.64	208	66.5	6.59	14.82
$CuSO_4$[d]	0.072	56.39	249	67.7	6.52	14.99
$MgSO_4$[e]	0.078	53.03	157	64.3	6.62	14.90
$MnSO_4$	0.091	52.05	191	69.4	7.67	14.94
$NiSO_4$[d]	0.067	54.02	211	59.9	4.61	14.74
$ZnSO_4$[d]	0.083	53.04	199	60.9	5.05	14.81

[a]Units: a_+, nm; λ^∞, S cm^2 mol^{-1}; K_A, dm^3 mol^{-1}; ΔS_A^0, ΔH_A^0, $\Delta H^\#$, kJ mol^{-1} [b]Ref.[18]; [c]Ref.[29]; [d]Ref.[3]; [e]Ref.[1]

In the same sense can be interpreted the lower value for Eyring's enthalpy of activation of charge transport found for Ca^{2+} ($\Delta H^{\#} = 13.94$ kJ mol^{-1}).

The higher value of λ^{∞} (1/2 Cu^{2+}) could be interpreted as a consequence of the more expressed hydrolysis. The equilibrium constant for the hydrolysis reaction of Cu^{2+} ion is the biggest among the divalent metal cations (3×10^{-8}) namely.[33]

Neglecting the value obtained for $CaSO_4$ aqueous solutions the average value of Eyring's enthalpy of activation of charge transport is, $\Delta H^{\#} = 14.8 \pm 0.1$ kJ mol^{-1} for all other discussed divalent metals sulfates. This finding is in agreement with the fact that $\Delta H^{\#}$ usually depends on the solvent properties mainly.

Entropies $\Delta S_A{}^0$ of ion pair formation, resulting form the temperature dependence of K_A are very close together for all discussed salts. Otherwise constant, K_A, and enthalpies $\Delta H_A{}^0$ of ion pair formation show more deviations but are still in reasonable agreement.

6. Concluding Remarks

It is evident that all investigated divalent metal sulfates exhibit very similar properties in diluted aqueous solutions. Recent investigations of the concentrate aqueous solutions of $MgSO_4$, $CoSO_4$, $NiSO_4$ and $CuSO_4$ by dielectric relaxation spectroscopy[2,4,34] suggest that the chief difference among these solutions could be in the formation of triple ions. They form only in concentrated solutions therefore it is necessary to extend the conductivity measurements on the concentrated solutions to determine whether some more definitive rules can be derived.

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8. References

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Povzetek

Izmerili smo električno prevodnost razredčenih vodnih raztopin kalcijevega in manganovega sulfata v temperaturnem območju med 5 in 35 °C v območju koncentracij $2 \times 10^{-4} < c/\text{mol dm}^{-3} < 5 \times 10^{-3}$. Na osnovi kemijskega modela smo določili vrednosti molskih prevodnosti pri neskončnem razredčenju, Λ^{∞}, ter konstante asociacije ionov, $K_{A,}$ v posameznem sistemu. S pomočjo znanih vrednosti limitnih prevodnosti sulfatnega iona smo ocenili limitne prevodnosti kalcijevega in manganovega kationa. Dobljene vrednosti smo primerjali z vrednostmi ostalih dvolentnih kovinskih kationov.