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The Representation of Electrical Conductances for Polyvalent Electrolytes by the Quint–Viallard Conductivity Equation

Part 7. Unsymmetrical 1:2 Type Electrolytes. Alkali Metal (Li, Na, K, Rb and Cs) Sulfates and Ammonium Sulfate

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Abstract Electrical conductivities of dilute aqueous solutions of lithium, sodium, potassium, cesium, rubidium and ammonium sulfates were determined and analyzed in terms of partially associated electrolytes of the 1:2 type. The conductivities reported here were determined from 15 to 35 °C and are compared with available literature results. Representation of conductances, in a framework of the ion association model, was performed using the Quint–Viallard conductivity equation and the Debye–Hückel expression for activity coefficients. However, the equilibrium constants were considered as adjustable parameters. Specific conductivities in concentrated aqueous solutions of sulfates were fitted to a new empirical equation with only three adjustable parameters. These parameters at constant temperature are much easier to determine from experimental conductivities than the corresponding four parameters in the usually applied Casteel and Amis conductivity equation.

Keywords Electrical conductances · Lithium sulfate · Sodium sulfate · Potassium sulfate · Cesium sulfate · Rubidium Sulfate · Ammonium sulfate · Ion equilibrium association constants

1 Introduction

The representation of electrical conductance in aqueous solutions, in pure organic solvents and in mixed solvents has been considered in the series of papers written by the present author [1–5]. Various types of electrolytes were discussed and they included the

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symmetrical electrolytes of the type 2:2 and 3:3 (alkali earth sulfates, transition metal sulfates, rare earth hexacyanoferrates(III) and hexacyanocobaltates(III)) and the unsymmetrical electrolytes of the type 3:1, 1:3, 3:2, 4:1, 4:1, 4:2, 2:4, 1:5, 6:1 and 1:6 (rare earth salts, cyanides, phosphates and various other salts). A new group of unsymmetrical electrolytes of the type 1:2, the aqueous solutions of alkali metal sulfates and of ammonium sulfate, are considered here.

Alkali metal sulfates, which are very soluble in water, can be found in large quantities near the surface of the earth and at least three of them, sodium sulfate, potassium sulfate and ammonium sulfate are produced in large quantities. They serve as main components or additives to fertilizers, Portland cements, glasses, food products, detergents and other manufactured goods. Numerous applications, in the Kraft process of wood pulping to produce paper, in heat storage in passive solar heating systems, in textiles and starch production, in purification of proteins, in promotion of catalytic activity and in many other areas are mentioned in the literature. It is worthwhile to point out that lithium sulfate, like other lithium salts, is employed as a drug to treat people suffering from the bipolar disorder (depression) and cesium sulfate is used to prepare dense aqueous solutions which are applied in density-gradient centrifugation.

Physicochemical properties of aqueous solutions of alkali metal sulfates have been extensively investigated, especially their thermodynamic properties (see for example [6–16]) and mainly these studies were directed to sodium and potassium sulfates. With only few exceptions, considering importance of alkali metal sulfates in chemical industry, determination of electrical conductivities started rather early but practically always measurements were performed in moderately or highly concentrated solutions, at high temperatures and pressures [6, 9, 10, 13, 17–27]. This fact and the absence of conductivity equations to represent dilute solutions of 1:2 type unsymmetrical electrolytes prevented the analysis of conductances in alkali metal sulfate solutions. There was no particular interest in determining conductivities of alkali metal sulfates in dilute aqueous solutions because the limiting conductance at infinite dilution $\lambda^0(\mathrm{Me}^+)$ of cations ($\mathrm{Me}^+ = \mathrm{Li}^+$, Na^+, K^+, Cs^+ and Rb^+) and the sulfate anion $\lambda^0(\mathrm{SO}_4^{2-})$, were well known from measurements in numerous systems with these ions (Table 1). However, it is clear from available data that

Table 1 Densities, *d*, viscosities, η, dielectric constants, *D*, of pure water and limiting ionic conductivities of ions, λ^0 [a] [37]

Θ/°C	15.00	20.00	25.00	30.00	35.00
d	0.99910	0.99821	0.99705	0.99565	0.99404
$\eta \times 10^3$	1.1382	1.0020	0.8903	0.7975	0.7195
D	82.039	80.176	78.358	76.581	74.846
$\lambda^0(\mathrm{Li}^+)$	30.20	34.37	38.68	43.18	48.00
$\lambda^0(\mathrm{Na}^+)$	39.77	44.81	50.10	55.72	61.54
$\lambda^0(\mathrm{K}^+)$	59.66	66.44	73.50	80.76	88.21
$\lambda^0(\mathrm{Rb}^+)$	63.44	70.50	77.81	85.00	92.91
$\lambda^0(\mathrm{Cs}^+)$	63.16	70.60	77.26	84.85	92.16
$\lambda^0(\mathrm{NH}_4^+)$	58.73	65.72	73.55	80.79	88.72
$\lambda^0(1/2\mathrm{SO}_4^{2-})$	62.72	71.10	80.02	89.33	99.03

[a] Units: d g·cm^{-3}; η Pa·s; λ^0 S·cm^2·mol^{-1}

in dilute aqueous solutions alkali metal sulfates do not always behave as strong 1:2 type electrolytes and therefore they were discussed in terms of the ionic association and changes in the degree of ion hydration [28, 29]. The main attention in analyzing properties of alkali metal sulfate solutions has been directed to concentrated solutions, namely to the importance of the cation hydration numbers and the ion/water ratios associated with the position of maximum values of specific conductivities and their shift as a function of temperature and concentration [23, 26].

Since 1978, with the appearance of the Lee–Wheaton (LW) [30, 31] and the Quint–Viallard (QV) [32–35] conductivity equations it was possible to represent conductances of unsymmetrical electrolytes in an adequate way, but these equations were rarely applied and never in the case of 1:2 type electrolytes.

In this investigation, the measured conductivities of dilute aqueous solutions of alkali metal sulfates, together with available values from the literature, were analyzed using the Quint–Viallard conductivity equation and the Debye–Hückel expression for activity coefficients. The determined ion association constants $K_A(T)$, treated as adjustable parameters, are also reported. The representation of conductivities in concentrated solutions was performed by replacing the usually used Casteel and Amis conductivity equation with its four adjustable parameters by a new conductivity equation. The proposed new equation gives excellent fitting to experimental conductivities, is mathematically simpler than the Casteel and Amis equation and has only three adjustable parameters.

2 Experimental

Sodium sulfate, rubidium sulfate and cesium sulfate (all better than 0.99 mass fraction and lithium sulfate 0.985 mass fraction) were purchased from Sigma Aldrich. Potassium sulfate and ammonium sulfate (all better than 0.99 mass fraction) were from Merck. All sulfates were used without further purification. Since lithium sulfate is hydroscopic, the solution samples of this and other reagents used here were prepared under isopiestic conditions. Salts were dissolved in water in a glove box where the vapor pressure of water was fixed to that of saturated solutions (for details see [36]). Solutions were prepared by weight by dissolving these reagents in double distilled water.

Electrical conductivities of solutions were determined using a glass cell (with a cell constant of 27.4 cm^{-1}) which was immersed in thermostated bath (± 0.01 K). The cell was calibrated with dilute potassium chloride solutions [37]. The resistances were determined with the help of a Wayne–Kerr Universal Bridge, model B211 [38]. Specific conductances κ were corrected by taking into account impurities dissolved in water (specific conductance less than about 2×10^{-7} $\text{S}\cdot\text{cm}^{-1}$). The molar conductances were calculated from $\Lambda = 1000\kappa\cdot c^{-1}$. Conversion from molal m to molar c units in dilute solutions was performed by using densities of pure water [37]. In the case of sodium sulfate solutions, their densities were correlated by $d_w(T)/(1 - d_w(T)f)$ where $d_w(T)$ is density of water at T and $f = 0.98871w - 0.28642w^2$ where w is the mass fraction of the salt.

Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within ± 0.3%.

3 Results and Discussion

3.1 Conductivity Equations

Molar conductance of an electrolyte $\Lambda(c,T)$ is the sum of ionic contributions $\lambda_j(c,T)$

$$\Lambda(c,T) = \frac{1000\kappa}{c} = \sum_j \frac{|z_j| c_j \lambda_j(c,T)}{c} \qquad j = \mathrm{Me}^{z+}, \quad \mathrm{SO}_4^{z-} \tag{1}$$

where κ is the measured specific conductance, z_j are the corresponding charges of the cation and anion ($z_+ = 1$ and $z_- = -2$) and c_j are their molar concentrations. The ionic conductances $\lambda_j(c,T)$ are represented by the following equation:

$$\lambda_j(c,T) = \lambda_j^0(T) - S_j(T)\sqrt{I} + E_j(T) I \ln I + J_{1j}(T) I - J_{2j}(T) I^{3/2} \qquad I = \frac{1}{2}\sum_j z_j^2 c_j \tag{2}$$

where the coefficients S_j, E_j, J_{1j} and J_{2j} are complex functions of the limiting equivalent ionic conductances λ_j^0, the distance parameters a_j and the physical properties of water (dielectric constant $D(T)$ and viscosity $\eta(T)$). These coefficients are available from the Quint–Viallard theory [32–35] (for explicit expressions see also [39]).

Without going into exact details about steps and mechanism of ion pairing process, if electrolytes are assumed to be partially associated, then the formal analytical concentration of solution c can be replaced by $c\alpha$ where α is the fraction of "free" ions and $c(1 - \alpha)$ denotes non-conducting (uncharged) particles. Thus, $\alpha = 1$ defines the fully dissociated electrolyte (the "strong electrolyte"). Evaluation of α for a given c (the so-called chemical problem) leads to the overall association constant K_A, which represents some kind of the apparent thermodynamic equilibrium constant. This constant can determined from the following mass-action equilibrium equation:

$$K_A(T) = \frac{1 - \alpha(c,T)}{v_+ v_- c(T) \alpha^2(c,T)} F(c,T) \qquad F(c,T) = \frac{f_{\mathrm{MeY}}(c,T)}{f_{Me^{z+}}(c,T) f_{Y^{z-}}(c,T)} \tag{3}$$

where v_+ and v_- are the stoichiometric coefficients (in the present case $v_+ v_- = 2$), f_j are the activity coefficients of individual ions (f_{MeY} is assumed to be unity) and they are approximated in dilute solutions by the Debye–Hückel expression:

$$\log_{10}[f_j(c,T)] = -\frac{z_j^2 A(T)\sqrt{I}}{1 + a_j B(T)\sqrt{I}} \tag{4}$$

At given absolute temperature T, constants $A(T)$ and $B(T)$ depend on dielectric constant of pure water

$$\begin{aligned} A(T) &= \frac{1.8246 \times 10^6}{[D(T)T]^{3/2}} \\ B(T) &= \frac{50.29 \times 10^8}{[D(T)T]^{1/2}} \end{aligned} \tag{5}$$

Values of the ion size parameters a_j in Eq. 4 were recommended by Kielland [40] and they are $a(\mathrm{Li}^+) = 6.0$ Å, $a(\mathrm{Na}^+) = a(\mathrm{K}^+) = 3.0$ Å, $a(\mathrm{NH_4}^+) = a(\mathrm{Rb}^+) = a(\mathrm{Cs}^+) = 2.5$ Å and $a\ (\mathrm{SO}_4^{2-}) = 4.0$ Å. The ion size parameters were assumed to be independent of temperature T. In the conductivity equations, the distance parameters were taken as a half sum of sizes of cation and anion.

At each temperature T, combining the chemical and conductance problems (the mass-action and QV equations), the experimental sets of conductivities can formally be written as $(\Lambda, c) = f(K_\mathrm{A}, \Lambda^0, a_j, D, \eta, c)$ and solved by an optimization procedure to give the K_A value that will assure the best fit between the experimental and the calculated conductivities. Iterations start with $\alpha = 1$ value in solving the quadratic equation:

$$\alpha(c,T) = \frac{1}{2}\left[-\frac{F(c,T)}{2K_\mathrm{A}(T)c(T)} + \sqrt{\left(\frac{F(c,T)}{2K_\mathrm{A}(T)c(T)}\right)^2 + \frac{2F(c,T)}{K_\mathrm{A}(T)c(T)}}\right] \tag{6}$$

where values of a_j, $D(T)$ and $\eta(T)$ and $\Lambda^0(T)$ are known. Iterations are stopped when the average standard deviation $\sigma(\Lambda)$ has a minimal value:

$$\sigma(\Lambda) = \sqrt{\frac{\sum_{i=1}^{N}\left(\Lambda_{i,\exp} - \Lambda_{i,calc}\right)^2}{N-1}} \tag{7}$$

where N denotes the number of experimental points.

In the present formulation, the mass-action equation takes the simplest mathematical form, but K_A is treated as an adjustable parameter. Evidently, if a particular mechanism of ion association is considered, the corresponding mass-action equation will be much more complex than Eq. 3 and the equilibrium constant will have a distinct physical meaning. Thus, in this representation, values of K_A give only an indirect indication about the existence of the ion association in electrolyte solutions.

3.2 Lithium Sulfate

Determination of electrical conductances in a few aqueous solutions of lithium sulfate started in 1879 and they are presented in the classical book of Kohlrausch and Holborn from 1898 [17]. More complete measurements were performed by the Jones group in 1912 [18] (determinations were performed by Dr. Jacobson and Dr. West). These measurements covered the 0–65 °C temperature range and the 0.0005 $\mathrm{mol \cdot dm^{-3}}$ to 0.5 $\mathrm{mol \cdot dm^{-3}}$ concentration range. In order to compare these conductances with the modern values they should be multiplied by factor 1.066 [41]. The next determinations were performed only in 1953 by Indelli [21] who reported lithium sulfate conductances at 25 °C from 0.004 $\mathrm{mol \cdot dm^{-3}}$ to 0.66 $\mathrm{mol \cdot dm^{-3}}$ and, in 1970, by Postler [42] from 0.005 $\mathrm{mol \cdot dm^{-3}}$ to 2.5 $\mathrm{mol \cdot dm^{-3}}$. The pressure effect on conductivities up to 2000 atmospheres, in the 0.00012 to 0.005 $\mathrm{mol \cdot dm^{-3}}$ concentration range, was reported by Fisher and Fox [27]. Electrical conductivities of concentrated and saturated lithium sulfate solutions were presented by Maksimova et al. [10] from 20 to 90 °C, Valyashko and Ivanov [23] from 25 to 75 °C and Cartón et al. [25] from 10 to 25 °C. Conductances of aqueous solutions of lithium sulfate at elevated temperatures are reported by Sharygin et al. [24].

Molar conductances in dilute solutions of lithium sulfate, from 0.00015 to 0.028 mol·dm^{-3} in the 15 to 35 °C temperature range, were determined in the present investigation and are reported in Table 2. As can be observed in Figs. 1 and 2, there is a reasonable consistency between the literature data in dilute and in concentrated solutions in spite of difficulties to work with hygroscopic lithium sulfate.

However, there is no doubt (Fig. 1) that all of the available literature conductivities in dilute concentrations at 25 °C differ considerably from those expected from the Onsager equation for strong electrolytes of the 1:2 type [35]:

$$\Lambda(c;T) = 2\left[\lambda_+^0(T) + \lambda_-^0(T)\right] - \left[\frac{1.1204\times 10^7 q\left[\lambda_+^0(T) + \lambda_-^0(T)\right]}{[D(T)T]^{3/2}(1+\sqrt{q})} + \frac{247.50}{\eta[D(T)T]^{1/2}}\right]\sqrt{I}$$
$$q = \frac{2\left[\lambda_+^0(T) + \lambda_-^0(T)\right]}{3\left[2\lambda_+^0(T) + \lambda_-^0(T)\right]} \tag{8}$$

As can be seen in Fig. 1, the proposed molecular model is valid only for the limited range of concentrations $c < 0.005$ mol·dm^{-3} and, in very dilute solutions, $c < 0.0001$ mol·dm^{-3}, a large scattering of experimental conductances exists. It is observed that the association constant K_A which is evaluated from Eq. 3 varies linearly with temperature T

$$\begin{aligned} K_A(T)/\mathrm{dm}^3\cdot\mathrm{mol}^{-1} &= -228.24 + 0.8282(T/\mathrm{K}) \\ \mathrm{R}^2 &= 0.9984 \end{aligned} \tag{9}$$

In concentrated solutions of lithium sulfate, the agreement between conductances coming from different investigations is very satisfactory and this is illustrated in Fig. 2 where the specific conductivities $\kappa(c)$ at 25.0 °C are plotted as a function of square root of concentration c. The form of specific conductivity curves, the ion/water ratios associated with the position of maximum values, and their shift as a function of temperature and concentration is discussed in [23, 26, 43].

3.3 Sodium Sulfate

Electrical conductivities of sodium sulfate aqueous solutions are well documented in the literature [13, 17, 18, 44]. Old determinations of Kohlrausch from 1879, performed at 18 °C are presented in his book [17]. Dr. Winston and Dr. Clover from the Jones group [18] in 1912, measured conductances in the 0–65 °C temperature range and from 0.0002 to 0.25 mol·dm^{-3}. Data for concentrated solutions from the few investigations in the 1879–1921 period are tabulated by Timmermans tables [44]. Actually, only the Bachofner thesis from 1904 is of importance [44], it includes specific conductances in the 0.1 to 1.25 mol·dm^{-3} concentration range, and from 20 to 80 °C. Modern determinations in dilute solutions, in the 1950 to 1981 period, all at 25 °C only, include investigations of Jenkins and Monk [20] (from 0.00005 to 0.0006 mol·dm^{-3}), Indelli [21] (from 0.0004 to 0.27 mol·dm^{-3}), Broadwater and Evans [22] (from 0.0003 to 0.0022 mol·dm^{-3}, also in D_2O and at 10 °C), Fisher and Fox [6] (from 0.00056 to 0.06 mol·dm^{-3} and at pressures up to 2000 atm) and Vivo et al. [43] (from 0.00045 to 0.0028 mol·dm^{-3}). Our measurements

Table 2 Experimental molar conductivities of aqueous solutions of alkali metal sulfates as a function of concentration m and temperature T

Λ/S·cm^{2}·mol^{-1}					
m/mol·kg^{-1}	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C
Lithium sulfate					
0.000150	177.0	199.9	223.8	248.7	275.4
0.000201	176.4	199.1	223.2	247.9	273.8
0.000502	174.8	198.1	220.7	243.2	268.9
0.000903	173.5	196.3	218.6	242.0	265.3
0.001103	171.5	195.2	217.5	241.0	263.7
0.001204	170.7	192.6	215.7	239.7	264.6
0.001505	169.3	192.1	213.8	237.1	262.7
0.001756	169.1	190.0	212.5	236.0	261.0
0.001996	168.2	189.8	212.2	235.9	260.8
0.002297	166.6	187.7	211.1	233.9	258.6
0.002699	164.9	185.9	208.7	231.8	256.5
0.003000	164.5	184.6	205.6	228.5	253.9
0.003502	163.6	183.4	203.9	227.2	250.3
0.004004	162.5	182.6	202.5	225.2	249.1
0.004987	160.9	180.1	199.8	221.6	245.7
0.007006	156.1	175.5	197.4	219.5	241.6
0.009809	152.2	170.5	192.2	213.1	235.6
0.020003	146.1	163.2	183.2	203.3	224.8
0.028301	137.9	157.7	175.8	196.7	216.4
Sodium sulfate					
0.00021	203.9	228.4	254.0	282.7	310.0
0.00030	202.3	226.9	252.6	281.1	308.8
0.00039	200.7	225.8	250.5	279.5	306.6
0.00051	198.8	223.4	248.9	276.5	304.4
0.00062	197.7	222.5	247.7	275.3	302.8
0.00071	197.3	222.0	247.0	275.4	302.6
0.00077	196.8	221.3	246.7	274.1	302.0
0.00093	195.9	221.4	244.3	273.5	304.1
0.00099	195.2	219.9	245.4	271.9	302.4
0.00193	189.6	213.8	239.1	266.0	292.7
0.00497	181.6	205.0	226.8	252.4	277.5
0.00711	175.6	197.9	220.3	245.0	270.4
0.00997	171.2	193.3	215.7	239.8	263.3
0.0200	163.0	185.1	205.9	228.2	249.2
0.0500	144.8	164.2	186.1	206.0	226.6
0.1000	130.2	147.1	165.8	185.9	201.7
0.2000	117.0	132.6	146.1	162.9	178.2
0.3999	100.1	113.4	126.7	139.4	153.4
0.4994	94.8	107.7	122.1	132.0	145.5
0.5998	90.3	101.6	113.3	126.1	138.8

Table 2 continued

Λ/S·cm^2·mol^{-1}					
m/mol·kg^{-1}	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C
0.7997	81.9	93.2	103.9	115.0	127.1
0.9994	75.4	85.4	95.5	106.5	117.5
1.2035	69.7	79.3	88.9	98.6	109.3
1.3978	64.9	73.9	82.9	92.4	102.8
Potassium sulfate					
0.000267	240.8	270.4	300.6	330.5	363.7
0.000416	239.0	267.9	296.5	329.4	360.7
0.000488	236.5	264.9	295.0	325.9	357.6
0.000623	235.0	262.5	292.8	324.5	356.4
0.000714	234.2	260.2	291.3	322.4	352.3
Rubidium sulfate					
0.000100	248.2	278.2	309.1	339.3	372.9
0.000150	247.7	277.1	308.4	337.8	371.5
0.000200	247.5	277.2	307.3	337.5	370.8
0.000300	245.6	274.8	304.8	335.1	367.6
0.000399	244.1	274.0	303.9	334.6	366.7
0.000500	242.9	271.7	301.1	331.0	363.4
0.000600	241.5	270.0	299.3	329.4	361.9
0.000700	240.2	268.5	298.0	327.7	359.9
0.000801	238.6	266.3	295.5	325.0	356.7
0.000900	237.9	266.1	295.3	324.8	355.8
0.001000	237.3	264.8	293.7	323.4	355.5
0.001200	236.0	263.9	293.3	321.9	352.3
0.001494	234.6	261.9	289.4	319.8	350.1
0.002000	231.1	258.6	287.1	316.3	346.3
0.002500	228.4	254.6	283.4	311.6	341.8
0.003482	225.4	251.7	279.0	307.3	336.0
0.004991	221.0	246.6	273.6	301.0	328.9
0.005801	219.2	244.5	271.2	298.3	326.7
0.006999	216.7	241.9	268.1	294.9	322.8
0.008501	213.4	238.1	264.0	290.3	317.6
0.009998	211.3	236.0	260.5	286.5	314.5
Cesium sulfate					
0.000399	244.5	273.3	303.6	334.4	366.1
0.000500	243.7	272.4	302.6	333.2	365.0
0.000600	243.2	271.7	301.9	332.3	364.2
0.000700	242.8	271.1	301.0	331.6	363.4
0.000800	241.5	269.6	299.2	329.4	361.0
0.000899	240.2	268.2	297.7	327.8	359.3
0.000999	239.0	266.9	296.1	325.9	357.2
0.002000	232.9	259.8	288.5	316.7	347.7
0.005000	220.6	247.5	274.0	300.9	329.7

Table 2 continued

Λ/S·cm^2·mol^{-1}					
m/mol·kg^{-1}	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C
0.006999	216.1	240.9	267.5	294.1	322.1
0.009999	210.2	234.3	260.1	286.3	312.8
Ammonium sulfate					
0.000250	237.8	268.1	297.7	329.8	361.8
0.000300	236.8	266.0	296.8	327.6	360.2
0.000400	235.2	264.3	294.8	325.6	357.1
0.000500	234.1	262.7	293.3	323.6	355.5
0.000600	233.0	261.9	292.4	322.5	354.8
0.000700	232.2	260.8	291.0	321.0	353.0
0.000800	231.8	260.2	290.3	320.3	350.2
0.000900	231.0	259.6	289.5	319.5	350.3
0.001000	229.8	258.1	288.3	317.4	348.9
0.001250	230.2	257.2	287.0	316.4	347.0
0.001500	227.3	255.2	284.8	314.1	345.1
0.001750	225.7	253.9	282.4	312.7	340.2
0.002000	223.4	251.0	280.3	310.5	337.7
0.003499	219.0	246.3	274.5	304.7	331.0
0.004999	212.4	239.0	266.0	293.4	321.7
0.007010	208.2	233.8	262.0	287.9	316.1
0.009997	201.9	226.3	251.2	276.7	304.0

Expected uncertainty of molar conductance is about ± 0.5 S·cm^2·mol^{-1}

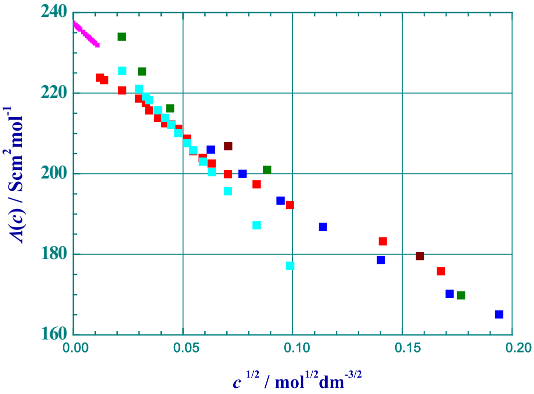


Fig. 1 Molar conductances of lithium sulfate aqueous solutions at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration *c*. *pink square*, fully dissociated 1:2 electrolyte; *dark green square*, [18]; *blue square*, [21]; *brown square*, [42]; *red square*, this work; *sky blue square*, calculated using the Quint–Viallard conductivity equation, this work (Color figure online)

cover dilute and moderately concentrated solutions (from 0.00021 to 1.4 mol·kg^{-1}) in the 15 to 35 °C temperature range (Table 2). Concentrated solutions of sodium sulfate were investigated by Valyashko and Ivanov [23] from 25 to 75 °C, Maksimova et al. [10] from 20 to 90 °C and Isono [9] from 15 to 55 °C.

As can be observed in Fig. 3, there is an excellent agreement between conductivities of sodium sulfate solutions coming from different investigations and in very dilute solutions they nearly behave as strong electrolytes of the 1:2 type. The association constants K_A have

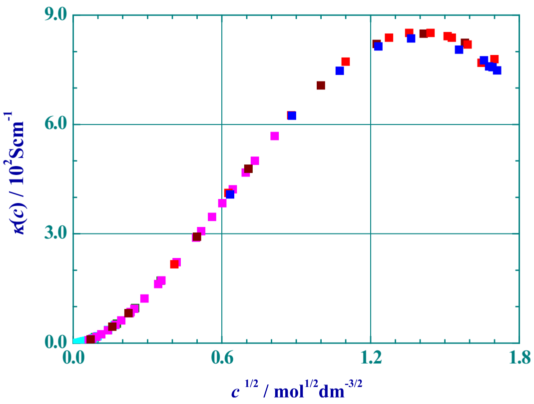


Fig. 2 Specific conductances of lithium sulfate aqueous solutions at 25.00 °C, $\kappa(c)$ as a function of square root of concentration c. *dark green square*, [18]; *pink square*, [21]; *red square*, [23]; *brown square*, [42]; *blue square*, [24]; *sky blue square*, this work (Color figure online)

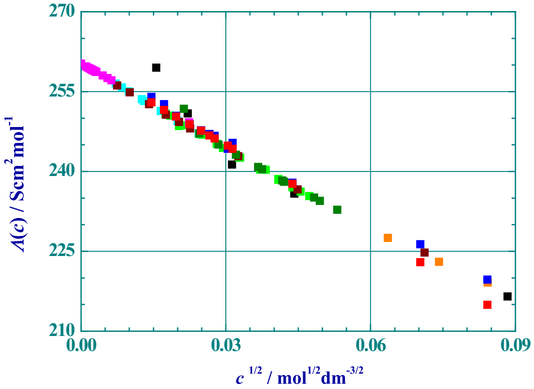


Fig. 3 Molar conductances of sodium sulfate aqueous solutions at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration c. *pink square*, fully dissociated 1:2 electrolyte; *brown square*, [6]; *black square*, [18]; *sky blue square*, [20]; *orange square*, [21]; *light green square*, [22]; *dark green square*, [45]; *blue square*, this work; *red square*, calculated using the Quint–Viallard conductivity equation, this work (Color figure online)

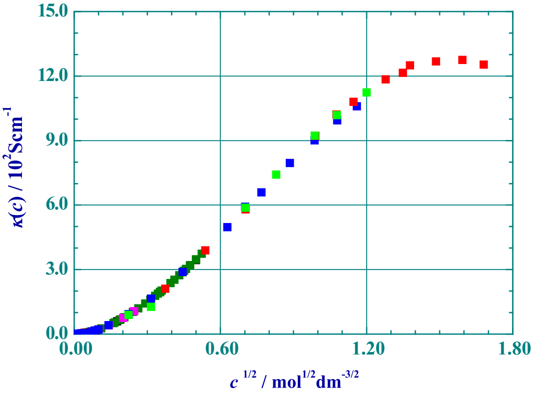
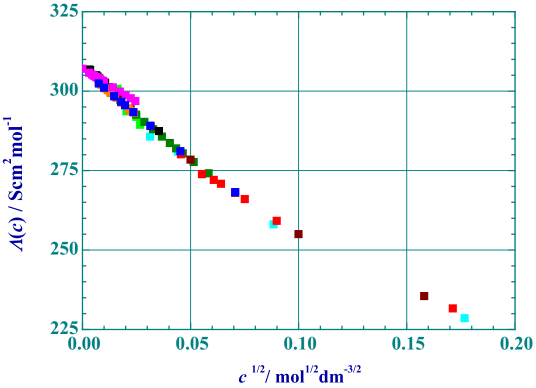


Fig. 4 Specific conductances of sodium sulfate aqueous solutions at 25.00 °C, $\kappa(c)$ as a function of square root of concentration c. *pink square*, [6]; *light green square*, [9]; *black square*, [18]; *sky blue square*, [20]; *dark green square*, [21]; *orange square*, [22]; *red square*, [23]; *brown square*, [45]; *blue square*, this work (Color figure online)

negligible values for concentrations lower than 0.0064 mol·dm^{-3} (as expected from the Onsager equation), and this is in an agreement with reported values in the literature [6]. Determined specific conductances in concentrated solutions of sodium sulfate are also in good agreement (Fig. 4).

Fig. 5 Molar conductances of potassium sulfate aqueous solutions at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration c. *Pink square*, fully dissociated 1:2 electrolyte; *sky blue square*, [18]; *brown square*, [19]; *orange square*, [20]; *red square*, [21]; *dark green square*, [22]; *blue square*, [26]; *black square*, [46]; *light green square*, this work (Color figure online)



3.4 Potassium Sulfate

Similar to the situation for sodium sulfate, the conductances of dilute aqueous solutions of potassium sulfate were reported in a number of investigations [17–22, 46]. Old measurements were performed by Klein in 1886 [17] and by Dr. West and Dr. Clover in 1912 [18] (in the 0–65 °C temperature range and from 0.00098 to 0.5 mol·dm^{-3}). Modern determinations at 25 °C started with measurements of transference numbers and conductances in 1937 by Hartley and Donaldson [46] (from 0.00048 to 0.0025 mol·dm^{-3}) and in 1941 by Fedoroff [19] (from 0.0001 to 0.65 mol·dm^{-3}). The next series of investigations in the 1950–1977 period includes these of Jenkins and Monk [20] (from 0.000057 to 0.00057 mol·dm^{-3}), Broadwater and Evans [22] (from 0.00031 to 0.0034 mol·dm^{-3}, also in D_2O and at 10 °C), Indelli [21] (from 0.0021 to 0.12 mol·dm^{-3}), and Fisher and Fox [26] (from 0.00005 to 0.05 mol·dm^{-3} and at pressures up to 2000 atm). Sharygin et al. [24] measured conductances of aqueous solutions of potassium sulfate at elevated temperatures. Reported here are new measurements from 15 to 35 °C in the 0.00027 to 0.0007 mol·dm^{-3} concentration range (Table 2). Concentrated solutions of potassium sulfate were determined only by Valyashko and Ivanov [23] from 25 to 75 °C and Maksimova et al. [10] from 20 to 90 °C. Unfortunately, they can not be compared because they were determined at different temperatures.

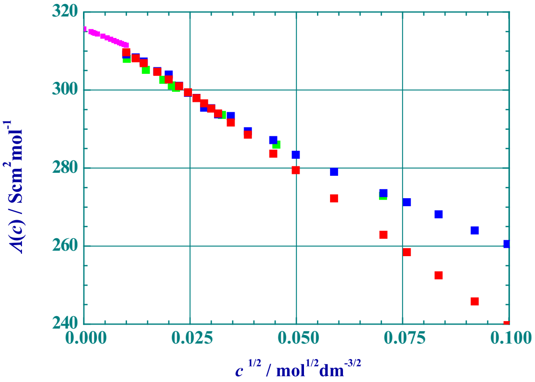
Molar conductances of aqueous potassium sulfate coming from different investigations are plotted in Fig. 5. As with sodium sulfate, potassium sulfate in very dilute solutions behaves as a nearly strong electrolyte of the 1:2 type. The association constants K_A have negligible values for concentrations lower than 0.0007 mol·dm^{-3}.

3.5 Rubidium Sulfate

Unlike the cases of sodium or potassium sulfates, electrical conductance studies in rubidium sulfate aqueous solutions are rare. In dilute solutions, there is only the investigation of Fisher and Fox [27] (at 25 °C, from 0.0001 to 0.005 mol·dm^{-3} and at pressures up to 2000 atm). Here, electrical conductivities, from 0.0001 to 0.01 mol·kg^{-1}, in the 15 to 35 °C temperature range are presented in Table 2.

Our measured conductivities of rubidium sulfate solutions at 298.15 K and the corresponding values from the Fisher and Fox investigation [27] are consistent and are plotted in Fig. 6. As can be observed, moderate association exists in rubidium sulfate solutions because $\Lambda(c)$ values deviate from those predicted for a fully dissociated electrolyte (from

Fig. 6 Molar conductances of rubidium sulfate aqueous solutions at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration c. *Pink square*, fully dissociated 1:2 electrolyte; *light green square*, [27]; *blue square*, this work; *red square*, calculated using the Quint–Viallard conductivity equation, this work (Color figure online)



Eq. 8). As for lithium sulfate, the association constant K_A depends linearly on temperature T

$$\begin{aligned} K_A(T)/\mathrm{dm}^3\cdot\mathrm{mol}^{-1} &= -460.00 + 1.600(T/\mathrm{K}) \\ \mathrm{R}^2 &= 0.9999 \end{aligned} \tag{10}$$

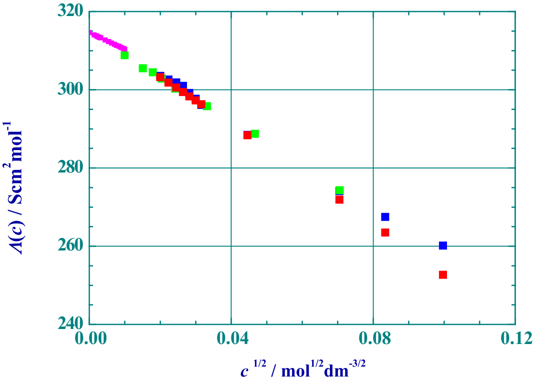
It follows from Eq. 10 that, at 15 °C, the association is small but increases strongly with temperature. The proposed model is valid only for a very dilute solutions $c < 0.001$ mol·dm^{-3}.

Few old measurements in concentration solutions of rubidium sulfate were tabulated in [44] and modern values in a wide temperature and concentration range were reported by Maksimova et al. [10] and Valyashko and Ivanov [23], but once again they can not be compared because their measurements were performed at different temperatures.

3.6 Cesium Sulfate

In dilute aqueous solutions of cesium sulfate, the electrical conductivities were reported only by Fisher and Fox [27] (at 25 °C, from 0.0001 to 0.005 mol·dm^{-3} and at pressures up to 2000 atm) and in the present investigation (from 0.0004 to 0.01 mol·kg^{-1}, in the 15 to 35 °C temperature range, see Table 2). If these conductivities at 298.15 K are compared with those calculated for the molecular model (Fig. 7) then it is evident that the association

Fig. 7 Molar conductances of cesium sulfate aqueous solutions at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration c. *Pink square*, fully dissociated 1:2 electrolyte; *light green square*, [27]; *blue square*, this work; *red square*, calculated using the Quint–Viallard conductivity equation, this work (Color figure online)



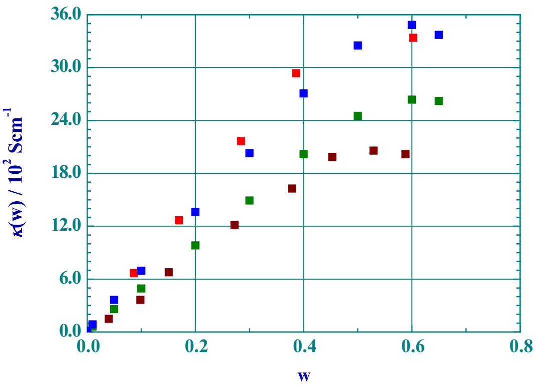


Fig. 8 Specific conductances of cesium sulfate aqueous solutions κ(w) as a function of the salt mass fraction *w*. 25.00 °C, *dark green square*, [10]; *brown square*, [47]; 50.00 °C, *blue square*, [10]; *red square*, [47] (Color figure online)

effect in aqueous solutions of cesium sulfate exists, but it is rather small. The effect is smaller than for rubidium sulfate, increases with T, but practically is negligible at low temperatures

$$\begin{aligned} K_{\mathrm{A}}(T)/\mathrm{dm}^3\cdot\mathrm{mol}^{-1} &= -119.96 + 0.394(T/\mathrm{K}) \\ \mathrm{R}^2 = 0.9999; &\quad T > 293.15\ \mathrm{K} \end{aligned} \tag{11}$$

The proposed molecular model is valid for $c < 0.002$ mol·dm^{-3}.

Specific conductivities in concentrated cesium sulfate were determined by Maksimova et al. [10], Valyashko and Ivanov [23] and Shilovskaya et al. [47]. Unfortunately, in the last investigation, they are presented only in graphical form. However, if the Shilovskaya et al. [47] conductivities are converted into a digital set and compared at the same temperatures (in Fig. 8) with those of Maksimova et al. [10], it is clear that both sets of data differ considerably, especially in very concentrated solutions of cesium sulfate.

3.7 Ammonium Sulfate

First measurements of conductances in aqueous solutions of ammonium sulfate were performed 1912 by Dr. Winston and Dr. Clover from the Jones group [18] (in the 0–65 °C temperature range and from 0.0002 to 0.5 mol·dm^{-3} concentration range). Scatchard and Prentiss [48] in 1932, determined conductances of ammonium sulfate solutions in the 0.0031 to 1.23 mol·kg^{-1} concentration range but only at 10 °C. In dilute solutions, their results are above the corresponding values calculated for the strong 1:2 type electrolyte (from Eq. 8). The electrical conductivities were reported also by Fisher and Fox [27] (at 25 °C, from 0.0001 to 0.005 mol·dm^{-3} and at pressures up to 2000 atm). The conductivities presented here (from 0.00025 to 0.01 mol·kg^{-1}, in the 15 to 35 °C temperature range) are given in Table 2. In concentrated solutions, the specific conductivities were determined only by Isono [49] (from 0.05 to 5.0 mol·kg^{-1}, in the 15 to 55 °C temperature range).

The available electrical conductances in dilute aqueous solutions of ammonium sulfate at 25 °C are plotted in Fig. 9. They are nearly consistent with behaviour of strong electrolyte of 1:2 type for $c < 0.001$ mol·dm^{-3}. Thus, as with sodium sulfate and potassium sulfate, in ammonium sulfate solutions the association effect is very small in dilute solutions..

The association constants K_{A} at 25 °C, determined in this investigation can be arranged in the following series $(NH_4)_2SO_4$, Na_2SO_4, $K_2SO_4 \ll Cs_2SO_4 < Li_2SO_4 < Rb_2SO_4$. The position of cesium sulfate in the above series is rather surprising, considering that cesium

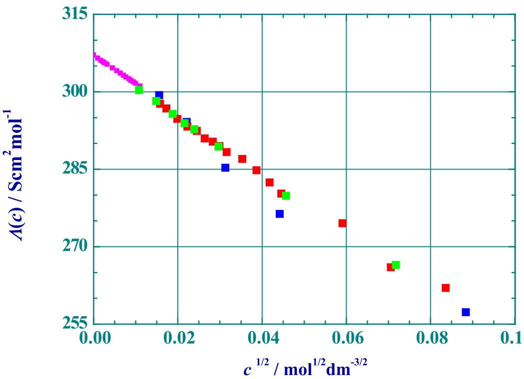


Fig. 9 Molar conductances of aqueous solutions of ammonium sulfate at 25.00 °C, $\Lambda(c)$ as a function of square root of concentration c. *pink square*, fully dissociated 1:2 electrolyte; *blue square*, [18]; *light green square*, [27]; *red square*, this work (Color figure online)

and rubidium cations have practically the same value of the limiting conductivities, $\lambda^0(\mathrm{Rb}^+) = 77.81$ S·cm^2·mol^{-1} and $\lambda^0(\mathrm{Cs}^+) = 77.28$ S·cm^2·mol^{-1}. It is worthwhile noting also the relatively large value of the limiting conductance of the sulfate anion $\lambda^0(1/2\mathrm{SO}_4^{2-}) = 80.02$ S·cm^2·mol^{-1} as compared with other anions. This is interpreted by a special mechanism of charge transfer in the case of sulfate anions [50] and therefore the cation–anion interaction can be different in each case. This is also true if hydration numbers of alkali metal ions are taken into account ($\mathrm{Li}^+ > \mathrm{Na}^+ > \mathrm{K}^+ > \mathrm{Cs}^+ > \mathrm{Rb}^+$ [37]).

Generally, the association constants of alkali metal sulfates and of ammonium sulfate are small, but also the upper limit of concentrations (usually $c < 0.001$ mol·dm^{-3}) where the applied molecular model can be used is also small. Thus, in dilute solutions of alkali sulfates, association exists, but in a different form then that expressed by Eq. 3. This is clearly indicated by a strong decrease in conductivity $\Lambda(c,T)$ with increasing c, as compared with that expected for corresponding strong electrolyte. In old papers, the formation of monovalent sulfate ion pairs (MeSO_4^-) was usually expressed in terms of dissociation constants K_d (formally, they are interrelated by $2K_\mathrm{A} = 1/K_\mathrm{d}$). The available in the literature values of K_d were determined by several experimental techniques and they lie in the following range $0.3 < \mathrm{p}K_\mathrm{d} < 1.0$ [51, 52]. They indicate only a small association and are consisted with K_A values reported here. However, there is not always agreement when pK_d series for(MeSO_4^-) ion pairs are presented. For example, at total molality $m = 0.1$ mol·kg^{-1}, at 25 °C, Reardon [52] proposed that pK_d can be arranged in the following way $\mathrm{HSO}_4^- > \mathrm{NH_4SO}_4^- > \mathrm{NaSO}_4^- > \mathrm{LiSO}_4^- > \mathrm{RbSO}_4^- > \mathrm{CsSO}_4^-$. Righellato and Davies [51] at 18 °C found that the degree of ion pairing increases for the series $\mathrm{LiSO}_4^- > \mathrm{NaSO}_4^- > \mathrm{KSO}_4^-$, but p$K_\mathrm{d}(\mathrm{RbSO}_4^-)$ and p$K_\mathrm{d}(\mathrm{CsSO}_4^-)$ are lower than for other sulfates, which gives a rather strange maximum value for KSO_4^-. Thus, there is no doubt that in aqueous solutions of monovalent sulfates the ion association is small, but for a particular alkali metal ion the exact strength of it continues to be questionable.

4 Concentrated Solutions of Monovalent Sulfates

Representation of the conductivities in dilute alkali metal and ammonium sulfates solutions using the Quint–Viallard conductivity equation is the main subject of this investigation. However, concentrated solutions are also important, especially from a practical point of view considering their industrial applications. Most determinations of specific conductances in concentrated solutions were performed by Valyashko and Ivanov [23], Isono [49] and especially by Maksimova et al. [10], but unfortunately their results are not easily accessible in the literature. Considering these circumstances, it is worthwhile presenting the specific conductances reported by above authors in a simple mathematical form.

The representation of specific conductivities of electrolytes in pure or mixed solvents is usually performed using the empirical equation proposed in 1972 by Casteel and Amis [53, 54]

$$\frac{\kappa(m)}{\kappa(m_{\max})} = \left(\frac{m}{m_{\max}}\right)^{a} \exp\left[b(m - m_{\max})^2 - a\left(\frac{m}{m_{\max}} - 1\right)\right] \tag{12}$$

At constant temperature T, the above equation includes four adjustable parameters a, b, $m_{\max}$ and $\kappa(m_{\max})$ and these parameters have no physical meaning. The last two parameters are not actual values of the maximum of specific conductivity and the corresponding concentration at which the maximum is situated. In many cases maxima do not exist at all or a broad maximum $\kappa(m_{\max})$ is observed, if the solubility is high enough to reach it. Thus, values of $m_{\max}$ and $\kappa(m_{\max})$ should also be determined by fitting procedures. Different concentration units can be used in the Casteel and Amis equation, molalities m can be replaced by molarities c or by mass fractions w ($0 < w < 1$).

The main disadvantage of the Casteel and Amis equation is that adjustable parameters must be derived using specially prepared computer programs. Unfortunately, an easy to use multivariate least-square method (e.g. Linest program in Excel) can not be applied. Thus, the Casteel and Amis equation or its logarithmic form cannot be reduced to the form

$$\kappa(w) = \sum_{i=1}^{N} a_i f_i(w) \tag{13}$$

where $f_i(w)$ are some known functions and a_i are adjustable parameters. Since the Casteel and Amis equation is a purely empirical equation, there is no reason not to use such functions $f_i(w)$ which are convenient in performing mathematical operations. Evidently, the simplest way to fit $\kappa(w)$ is to use polynomials of w with the imposed condition that $\kappa(w) = 0$ at $w = 0$

$$\kappa(w) = Aw + Bw^2 + Cw^3 + Dw^4 + \ldots \tag{14}$$

or in the form

$$\kappa(w) = aw^{1/2} + bw + cw^{3/2} + dw^2 + \ldots \tag{15}$$

However, there is a second possibility to replace the Casteel and Amis equation by applying the semi-theoretical approach in an interpretation of the temperature dependence of transport properties in glass-forming liquids and fused salts. Such an equation has the form of the modified Arrhenius equation (the Vogel–Fulcher–Tammann type equation [54])

$$\kappa(w, T) = \frac{Aw}{\sqrt{T}} \exp\left(-\frac{k}{T - T_0}\right) \tag{16}$$

where A and k are constants and T_0 is the glass-transition temperature. This equation was originally derived from the free volume theory of viscous liquids and is adapted to represent transport properties of concentrated electrolyte solutions.. At constant temperature

Table 3 Representation of specific conductivities in concentrated aqueous solutions of alkali metal sulfates at different temperatures, parameters of Eq. 21, A, B and C, $w_{\max}$, positions of maximum of specific conductivity, w^*, concentration region, and σ the standard mean deviation of specific conductivity

Θ/°C	A/S·m^{-1}	$-B$	C	$w_{\max}$	w^*	σ/Sm^{-1}	Ref.
Lithium sulfate							
25	128.30	5.803	1.021	0.184	0.26	0.11	[23]
50	200.94	6.282	4.042	0.223		0.16	
75	272.71	6.268	4.455	0.245		0.39	
20	104.90	4.693	−2.308	0.181	0.24	0.17	[19]
30	129.21	4.690	−1.691	0.188		0.16	
40	153.05	4.652	−1.138	0.196		0.21	
60	213.82	5.447	1.861	0.215		0.34	
80	262.68	5.199	2.015	0.235		0.34	
90	292.02	5.380	2.731	0.249		0.38	
Sodium sulfate							
25	185.39	12.627	37.386		0.20	0.70	[23]
50	287.12	12.604	38.463			1.14	
75	398.94	13.281	42.691			1.50	
20	102.83	4.160	5.074		0.20	0.20	[10]
30	125.59	3.755	3.261			0.07	
40	150.30	3.775	3.875			0.09	
60	201.98	3.847	4.964			0.37	
80	251.83	3.757	4.904			0.17	
90	276.76	3.769	5.116			0.20	
20	125.30	7.379	15.1307			0.07	
25	138.67	6.729	20.3411		0.17	0.12	[9]
30	153.36	6.729	15.4278			0.14	
35	168.44	6.741	15.7639			0.15	
45	199.50	6.794	16.4756			0.18	
55	231.74	6.858	17.0622			0.22	
Potassium sulfate							
25	130.62	6.753	42.104		0.09	0.15	[23]
50	197.67	6.420	33.674			0.11	
75	263.71	5.317	16.589			0.12	
20	116.45	5.032	25.402		0.10	0.09	[10]
30	145.12	5.724	28.538			0.10	
40	158.52	−4.004	−37.539			0.10	
60	229.53	6.482	31.536			0.16	
80	287.61	7.017	34.326			0.17	
90	312.37	6.777	31.786			0.12	
Rubidium sulfate							
25	77.23	0.956	1.749		0.31	0.12	[23]
50	115.98	1.238	1.977			0.18	
75	172.31	1.644	2.556			0.23	
20	71.24	0.989	1.985		0.30	0.07	[10]
30	86.24	1.096	2.054			0.09	

Table 3 continued

Θ/°C	A/S·m^{-1}	$-B$	C	$w_{\max}$	w*	σ/Sm^{-1}	Ref.
40	101.90	1.291	2.377			0.06	
60	132.45	1.253	1.943			0.11	
80	164.34	1.466	2.276			0.17	
90	179.93	1.520	2.314			0.19	
Cesium sulfate							
25	48.61	−0.821	−1.425	0.754	0.62	0.48	[23]
50	74.14	−0.497	−1.170	0.769		0.62	
75	100.18	−0.287	−0.999	0.783		0.72	
20	43.83	−1.078	−1.859	0.683	0.65	0.57	[10]
30	53.63	−0.906	−1.714	0.688		0.62	
40	63.80	−0.765	−1.592	0.693		0.66	
60	84.51	−0.563	−1.421	0.700		0.70	
80	104.37	−0.466	−1.357	0.699		0.77	
90	114.09	−0.441	−1.335	0.700		0.91	
Ammonium sulfate							
15	124.77	2.315	1.216		0.40	0.54	[49]
20	139.46	2.433	1.419			0.52	
25	154.54	2.539	1.602			0.58	
30	170.03	2.636	1.769			0.63	
35	185.78	2.722	1.913			0.68	
40	201.57	2.795	2.043			0.74	
45	217.70	2.871	2.180			0.80	
50	233.96	2.937	2.298			0.86	
55	250.47	3.004	2.411			0.92	

T, Angell [55–57] suggested that A and k are independent of composition and $T_0(w)$ can be related in electrolyte solutions with the help of a polynomial [54, 55–57]

$$T_0(w) = a + bw + cw^2$$

Actually, Angell used only the first two terms in the representation of electrical conductivities in concentrated solutions of electrolytes [56, 57].

Considering that $T_0/T < 1$ and $(T_0/T)^2 \ll 1$, the argument of the exponent can be written in the following form:

$$-\frac{k}{T - T_0} = -\frac{k}{T\left(1 - \frac{T_0}{T}\right)} = -\frac{k}{T}\left[1 + \frac{T_0}{T} + \left(\frac{T_0}{T}\right)^2 + \cdots\right] \tag{17}$$

and Eq. 16 becomes:

$$\begin{aligned} \kappa(w;T) &= \frac{Aw}{\sqrt{T}}\exp\left(-\frac{k}{T}\left[1 + \frac{T_0}{T}\right]\right) \\ &= \frac{\mathrm{A}w}{\sqrt{T}}\exp\left(-\frac{k}{T}\left[1 + \frac{a + bw + cw^2}{T}\right]\right) \end{aligned} \tag{18}$$

and finally, if the exponent is also expanded, this equation takes the simple form given by Eq. 14. If no exact physical meaning or values are associated with adjustable parameters in Eq. 18, then the representation of specific conductivities at constant T can be reduced to a simple equation having the form:

$$\ln\left[\frac{\kappa(w,T)\sqrt{T}}{w}\right] = \alpha + Bw + \mathrm{C}w^2 \tag{19}$$

Thus, the final new equation for electrical conductivities in concentrated solutions has only three A, B and C adjustable parameters

$$\begin{aligned} \kappa(w;T) &= A\,w \exp\left[Bw + Cw^2\right] \\ A &= \frac{e^{\alpha}}{\sqrt{T}} \end{aligned} \tag{20}$$

This equation gives an excellent representation of specific conductances and their parameters are easily available using its logarithmic form (Eq. 19). If the specific conductivity has a maximum,

$$\kappa(w_{\max},T) = A\,w_{\max} \exp\left[Bw_{\max} + Cw_{\max}^2\right] \tag{21}$$

then the maximum appears at the mass fraction given by

$$w_{\max}(T) = \frac{-B - \sqrt{B^2 - 8C}}{4C} \tag{22}$$

In Table 3 are presented A, B and C parameters for the monovalent cation sulfates considered here, w^* denotes the concentration region, $w_{\max}$ value (if it exists for the investigated sulfate) is calculated from Eq. 22 and finally the standard deviation of specific conductance $\sigma(\kappa(w))$, which gives an indication how the fit of experimental results by using Eq. 21 is good.

5 Conclusions

Electrical conductivities of dilute aqueous solutions of lithium, sodium, potassium, cesium, rubidium and ammonium sulfates were determined from 15 to 35 °C. The literature conductivities and those reported here are consistent. It was observed that sulfates can be represented in dilute solutions as strong electrolytes or partially associated electrolytes of the 1:2 type. Conductances were analyzed using an ion association model, which included the Quint–Viallard conductivity equation and the Debye–Hückel expression for activity coefficients. In this model, the calculated equilibrium constants were considered as adjustable parameters and can be arranged in the following series $(NH_4)_2SO_4$, Na_2SO_4, $Na_2SO_4 \ll Cs_2SO_4 < Li_2SO_4 < Rb_2SO_4$.

It was demonstrated that specific conductivities in concentrated aqueous solutions of alkali metal sulfates can be fitted to a new empirical equation with only three adjustable parameters. The proposed conductivity equation for specific conductivities is superior to the usually used Casteel and Amis equation with four adjustable parameters.

Acknowledgements Technical assistance of Paulina Veinner is very much appreciated.

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