Temperature Dependence of Association Constants of LiAlCl$_4$ in Liquid Sulfur Dioxide

Robert Hartl,[1] Roland Neueder[2] and Heiner J. Gores[1,*]

[1] *University of Regensburg, Institute for Theoretical and Physical Chemistry, Workgroup Electrochemistry and Electrolytes, 93053 Regensburg, Germany*

[2] *University of Regensburg, Institute for Theoretical and Physical Chemistry, 93053 Regensburg, Germany*

* *Corresponding author: E-mail: heiner.gores @chemie.uni-regensburg.de*

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

In this work the conductivities of LiAlCl$_4$ in dilute sulfur dioxide solutions were measured in the temperature range 238.15 K to 288.15 K. The major challenge of these measurements was the handling of the very water sensitive salt LiAlCl$_4$ and the formulation of sulfur dioxide solutions at low salt concentrations. These low concentration solutions are needed to obtain association constants of the salt and thermodynamic parameters using the low concentration chemical model developed by J. Barthel. The viscosities of liquid sulfur dioxide were also measured in the temperature range 231.46 K to 257.98 K. Unexpectedly, the determined association constants of LiAlCl$_4$ in liquid sulfur dioxide are very small ranging from 42 at 238.15 K to 354 dm^3 mol^{-1} at 288.15 K. This result shows that the lithium-ion solvent interaction is much stronger when compared with the interaction of the lithium-ion with the weakly coordinating anion tetrachloroaluminate, in contrast to lithium halides in liquid sulfur dioxide where association constants up to 96000 dm^3 mol^{-1} are observed.

Keywords: Non aqueous solutions, electric conductivity, lithium tetrachloroaluminate, ion association, sulfur dioxide

1. Introduction

Today, mobility is a key issue for everyone. Therefore we need efficient batteries, nowadays especially those based on lithium ion technology. Intensive research has increased the energy density and the power density of the first successfully introduced secondary lithium ion battery by Sony.[1] The conductivity of ion conductors in cells is the best studied key property for the performance of lithium ion cells. It determines voltage drop, power density as well as heat evolution. Therefore, conductivity is an important property for modelling lithium ion batteries.[2] Common secondary lithium ion batteries are based on organic solvents (LiPF$_6$ in a blend of organic carbonates).[3] Specific conductivities of electrolytes on the base of organic solvent vary from about 4 mS cm^{-1} to about 10 mS cm^{-1} [4] at ambient temperature. For reviews on electrolytes

for lithium and lithium-ion batteries, see Refs.[5,6] In addition, primary lithium batteries and secondary lithium ion batteries[7–9] based on inorganic solvents[10] were also developed (e.g. lithium/thionylchloride,[11–13] lithium/sulfur dioxide[13,14] and lithium/sulfuryl chloride[15,13] primary batteries). In lithium sulfur dioxide batteries, sulfur dioxide is the liquid cathode material. For secondary batteries based on SO$_2$ as the inorganic solvent the liquid cathode material used in primary Li/SO$_2$ cells was replaced by LiCoO$_2$[16–18] and a concentrated solution of LiAlCl$_4$ in sulfur dioxide with low vapour pressure is used as the electrolyte showing a very high specific conductivity of about 70 mS cm^{-1} at ambient temperature.[19] This secondary battery electrolyte has a unique property, it is not flammable.

In contrast to nearly every battery electrolyte, the conductivity of very dilute LiAlCl$_4$/sulfur dioxide solutions and the association behaviour of this electrolyte has not been studied up to now. We suppose that there is a

simple reason for that: The water content of available sulfur dioxide. Conductivity measurements at low concentrations are generally affected by traces of water. It should be stressed again here, that even water traces in the range of 20 ppm reach the order of a 1 mM solution. The effect of water can be indirect or direct. To give an example for an indirect effect, we already reported that 380 ppm water in $LiClO_4$/tetrahydrofurane (THF) solutions increased the conductivity by 51.7%. $LiClO_4$ does not react with water, but only a replacement of THF in the solvation sphere of the lithium ion shifts association equilibria and hence increases conductivity, c.f. Ref.[20,21] For $LiAlCl_4$/sulfur dioxide the situation is much worse as $LiAlCl_4$ directly reacts with water forming insoluble hydrolysis products and reducing the concentration of the salt. In order to perform reliable measurements for this electrolyte nearly water-free sulfur dioxide is needed.

Our conductivity studies were evaluated with the low-concentration chemical model (lcCM) developed by Barthel et al.[22] This model has the benefit to include non-Coulombic interactions. In addition, as numerous electrolytes have been evaluated with the lcCM (c.f. several books in the series: Electrolyte Data Collection, DECHEMA Chemistry Data Series, Frankfurt, Germany, by J. Barthel et al.) results for ion association of this salt can be easily compared with association behaviour of other electrolytes on the same basis.

2. Experimental

2. 1. Materials

Lithium tetrachloroaluminate was purchased from *Aldrich* (purity of 99.99%, water-impurity of < 100 ppm). It was used without any further purification. Sulfur dioxide was purchased from *Linde* (purity grade 99.98). The gas was condensed in a cryo-trap and stored over phosphorus pentoxide for at least 24 hours. Without drying, the subsequent solutions would become dully and a white precipitate appears indicating the hydrolysis of $LiAlCl_4$.

2. 2. Thermostat

The high precision thermostat used in the experiments has been described previously.[23] It can be set to each temperature of a temperature program with a reproducibility of less than 3 mK.

2. 3. Viscosity Measurement

The viscosity measurements of the pure sulfur dioxide were executed with the help of an Ubbelohde viscometer (AVS/G, *Schott*) placed in a Dewar flask connected via a circulating pump to the high precision thermostat. The dried sulfur dioxide was condensed into the measuring cell and the flow time was then measured automatically by the control unit (AVS/G, *Schott*). The temperature in the Dewar flask was controlled via a calibrated NTC and fluctuations do not exceed 3 mK during the whole measurement. The apparatus was described previously in more detail.[24]

2. 4. Conductivity Measurements

The conductivity measurements were performed in a home built conductance cell with a three electrode assembling. Because of the gaseous state of sulfur dioxide at ambient temperature, stock solutions could not be used for preparing the solutions. Hence, weighing vessels (glas) were filled with $LiAlCl_4$ in an argon glove box (*Mecaplex, Switzerland*) ($H_2O \leq 0.4$ ppm, $O_2 \leq 5$ ppm, Water-analyzer: Kurt Gerhard, Germany; O_2-analyzer: MBraun, Germany), then put into small aluminium vessels and sealed with a lid (o-ring made of perbunan). The weight of the vessels were determined with the help of a microbalance (AX26-Comparator, *Mettler-Toledo*). The glass vessel with the salt was then transferred into the conductance cell and an appropriate amount of liquid sulfur dioxide was condensed into the cell. The amount of the sulfur dioxide was determined by weighing. With this procedure the uncertainty of the concentration is estimated to be less than 0.3 %.

The filled conductance cell was immersed into the precision thermostat and after temperature equilibration the resistance of the solution was determined with the help of a Wheatstone bridge, for details see Ref.[23] The conductance cell was previously calibrated with dilute potassium chloride solutions as described in[25] and the cell constant was determined to be 0.17673 cm^{-1}.

3. Results and Discussion

3. 1. Viscosity Measurement

From the measured flow times the obtained kinematic viscosities ν were converted to dynamic viscosities η with the help of temperature dependent densities of liquid sulfur dioxide (calculated with an equation from Refs.[26,27]) and quoted in Table 2. The experimental results are summarized in Table 1. For the temperature dependence of the dynamic viscosities η(T) the Vogel-Fulcher-Tammann-equation:[28–30]

$$\eta(T) = \eta_0 \cdot \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

is usually used, where η_0, B and T_0 are adjustable parameters. A least-square fit of the data given in Table 1 yields $\eta_0 = 0.1959 \times 10^{-4}$ Pa s, B = 799.9 K, $T_0 = 9.82 \times 10^{-7}$ K. The standard deviation of the fit was 5.3×10^{-6} Pa s.

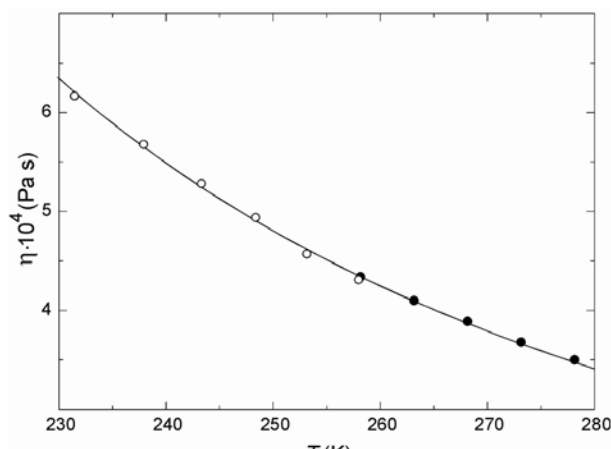Figure 1 compares our data with the data of Awbery and Griffiths[31] and with the calculated curve from Eq.(1).

Figure 1. Dynamic viscosity of liquid sulfur dioxide (O this paper, ● Ref.[31], line calculated with Eq. (1).

Table 1: Temperature dependent dynamic viscosity of pure sulfur dioxide

T/K	η 10^4/(Pa s)	T/K	η 10^4/(Pa s)
231.46	6.17	248.37	4.94
237.90	5.68	253.16	4.57
243.31	5.28	257.98	4.31

This Figure shows, that the parameters of Eq.(1) obtained from data at lower temperatures (T < 258 K) are in accordance with literature data at higher temperatures (T > 258 K). The viscosities used for the data analysis of the conductance data at different temperatures are calculated from Eq.(1).

3. 2. Conductivity Measurements

Measured conductivity data of LiAlCl₄ in liquid sulfur dioxide are given in Table 2. The data analysis is exe-

cuted with the help of a computer program, which was developed by Barthel, Popp, et al.[32] This program is based on the low-concentration chemical model (lcCM),[22] a Hamiltonian model at the MacMillan-Mayer level. This model uses the following set of equations

$$\frac{\Lambda}{\alpha} = \Lambda_0 - S(\alpha c)^{1/2} + E'\alpha c \ln(\alpha c) + \\ + J_1(R)\alpha c + J_2(R)(\alpha c)^{3/2} \tag{2}$$

$$\ln y'_\pm = -\frac{\kappa_D q_B}{1 + \kappa_D R} \tag{3}$$

$$K_A^{(c)} = \frac{(1-\alpha)y_{IP}}{\alpha^2 c y'^2_\pm} \tag{4}$$

where Λ and Λ_0 are the molar conductivities at molarity c and its limiting value, $(1-\alpha)$ is the fraction of oppositely charged ions acting as ion pairs, $K_A^{(c)}$ is the thermodynamic association constant in the molarity scale and $y'_\pm$ is the mean activity coefficient of the chemical model of electrolyte solutions for the dissociated part of the electrolyte (the so-called 'free' ions). The formulas for coefficients of Eq. (2) calculation are given in Ref.[22] $J_1(R)$ and $J_2(R)$ are functions of the parameter R which is the distance up to which oppositely charged ions are counted as non-conducting ion pairs and hence is also the upper limit of the ion-pair association constant K_A.

The Debye parameter κ_D and the Bjerrum parameter q_B of Eq.(3) are given by the following relationships (for 1.1-electrolytes):

$$\kappa_D^2 = \frac{2e_0^2 \alpha c}{\varepsilon_0 \varepsilon k_B T} \tag{5}$$

Table 2: Conductivity data of LiAlCl₄ in liquid sulfur dioxide.

c /(mol m⁻³)	$\Lambda \cdot 10^4$ /(S m² mol⁻¹)	c /(mol m⁻³)	$\Lambda \cdot 10^4$ /(S m² mol⁻¹)	c /(mol m⁻³)	$\Lambda \cdot 10^4$ /(S m² mol⁻¹)
T = 238.15, ε = 19.30[b], η = 5.63 10⁻⁴, ρ = 1.519[c]		T = 248.15, ε = 18.10[b], η = 4.92 10⁻⁴, ρ =1.495[c]		T = 258.15, ε = 16.95[b], η = 4.34 10⁻⁴, ρ = 1.471[c]	
1.283	91.6	1.263	103.2	1.242	114.0
1.767	90.0	1.738	100.8	1.710	110.7
2.349	86.4	2.311	96.4	2.274	105.5
3.420	83.3	3.366	92.5	3.311	101.0
4.749	80.8	4.673	89.5	4.597	97.0
T = 268.15, ε = 15.81[b], η = 3.87 10⁻⁴, ρ = 1.446[c]		T = 278.15, ε = 14.62[b], η = 3.48 10⁻⁴, ρ = 1.422[c]		T = 288.15, ε = 13.34[b], η = 3.15 10⁻⁴, ρ = 1.397[c]	
1.221	123.7	1.201	131.8	1.180	137.4
1.682	119.3	1.653	126.1	1.625	130.6
2.236	113.3	2.198	119.3	2.161	123.8
3.256	107.9	3.201	113.0	3.146	115.8
4.521	103.1	4.444	107.2	4.368	109.2

[a] Units: T, K; η, Pa s; ρ; kg dm⁻³; [b]Ref.[37]; [c]Ref.[26,27]

$$q_B = \frac{e_0^2}{8\pi\varepsilon_0\varepsilon k_B T} \qquad (6)$$

According to the chemical model of electrolyte solutions, the distance parameter R in Eqs.(2) and (3) is the sum of the crystallographic radius a and the length s of an orientated solvent molecule s ($R = a + s$). We used $R = 0.816$ nm in our calculations, a value obtained by Simon et.al.[33] from crystallographic studies of LiAlCl$_4$ × 3SO$_2$. Setting the coefficients S, E' and $J_1(R)$ in Eq. (2) to their theoretical values yields the quantities Λ_0, K_A and J_2 by a non-linear least squares iteration. The limiting conductivities Λ_0 and the association constants K_A are given in Table 3, together with the so-called Walden product ($\Lambda_0 \eta$). Figure 2 shows the experimental conductivities at different temperatures and the curves calculated with Eq.(2) and the parameters given in Table 3.

The distance parameter R calculated from the J_2-term was found within a range from 0.9 to 1.0 nm (input value 0.82 nm) and satisfies the compatibility condition.[34,35]

The decrease of the limiting molar conductivities Λ_0 with decreasing temperature is mainly due to increasing viscosity. This regular viscosity effect is reflected by an almost constant Walden product, which scatters around a value of 0.63×10^{-5} (Sm^2 Pa s mol^{-1}), c.f. Table 3. According to Stokes law, this constancy additionally indicates, that the hydrodynamic radii of the moving particles are independent of temperature. From single ionic conductivities published by Takezawa et al.[36] the transference number of Li$^+$ at 25 °C can be calculated ($t_{Li+} = 0.328$). If one further assumes its temperature independence, the limiting conductivity can be split into ionic contributions leading to the single ion conductivities given in Table 3.

The association constant of LiAlCl$_4$ in liquid SO$_2$ increases by one order of magnitude from 40 to 350 dm^3 mol^{-1} in the temperature range of this investigation (238–288 K). However, compared to other 1.1-salts, LiAlCl$_4$ shows a relatively small association constant. This result is favorable for the use of the electrolyte LiAlCl$_4$/SO$_2$ in an inorganic battery. Takezawa[36] determined association constants of LiBr and LiI in liquid sulfur dioxide which are two order of magnitude higher than that of LiAlCl$_4$ c.f. Table 4. Due to the low temperature dependent permittivity ε(SO$_2$) of about 13 to 20,[36,37] much higher association constants would be expected in this solvent for LiAlCl$_4$.

There is a simple reason for that. Generally, solvent molecules and anions compete for a coordination site at

Table 3: Limiting conductivity, association constant, Walden product and limiting single ion conductivities of LiAlCl$_4$ in SO$_2$.

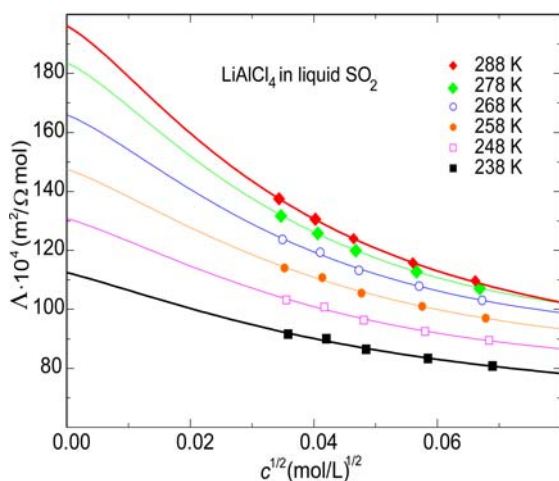| T /K	$\Lambda_0 \cdot 10^4$ /(S m^2 mol^{-1})	K_A /(S m^3 mol^{-1})	$\Lambda_0 \eta \cdot 10^5$ /(S m^2 Pa s mol^{-1})	$\lambda_0^+ \cdot 10^4$ /(S m^2 mol^{-1})	$\lambda_0^- \cdot 10^4$ /(S m^2 mol^{-1})
238.15	112.5	42	0.62	36.9	75.8
248.15	130.9	109	0.64	43.0	87.9
258.15	147.6	148	0.57	48.5	99.1
268.15	166.0	232	0.64	54.5	111.5
278.15	183.7	325	0.64	60.3	123.4
288.15	196.1	354	0.63	64.4	131.7

Figure 2. Molar conductivity of LiAlCl$_4$ in liquid sulfur dioxide at various temperatures, for details see text.

cations.[38,20] If the solvent molecule is an excellent ligand, depending on its donor properties and steric reasons and the anion is a weakly coordinating anion, association constants may be low despite a low dielectric permittivity of the solvent and vice versa. For example, despite the rather high dielectric permittivity of propylene carbonate (ε(PC) = 64.95)[20] lithium acetates show a very high association constant and even triple ions are observed.[40] In this case the anion is a bidentate ligand, and PC is a monodentate ligand and has a low donor number DN = 15,1 kcal mol^{-1}. For LiAlCl$_4$ / SO$_2$ nearly reverse situation is the reason for rather low association constants: SO$_2$ is a bidentate ligand an therefore is an excellent ligand, despite its low donor number of only DN = 6.5 kcal mol^{-1}.[39] The reason for this unexpected behaviour is the strong polarisation of the molecule by the small lithium ion. Tetrachloroaluminate is a weakly coordinating anion due to its four electron with-

Table 4: Association constants and molar limiting conductivity of some lithium salts.

Salt	T /K	ε	K_A /(dm³ mol⁻¹)	$\Lambda_0 \cdot 10^4$ /(S m² mol⁻¹)	Ref
LiBr in SO_2	273,15	15.35	33500	195.6	[36]
LiBr in SO_2	298.15	12.0	96100	226.8	[36]
$LiAlCl_4$ in SO_2	238.15	19.30	42	112.5	this work
$LiAlCl_4$ in SO_2	288.15	13.34	354	196.1	this work
LiI in SO_2	298.15	12.0	16600	194.2	[36]
$LiClO_4$ in 2-butanone	298.15	18.0	501.7	178.3	[41]
LiCl in 2-butanone	298.15	18.0	116787	153.1	[41]
$LiAlCl_4$ in methyl formate	298.15	8.9	88500	163.5	[42]

drawing chlorine atoms. The negative charge is distributed over the whole anion. Table 4 shows some association constants of some lithium salts in different solvents. Salts of weakly coordinating anions such as tetrachloroaluminate and perchlorate show much smaller association constants when compared with halogenides such as chloride, bromide or iodide. In methyl formate the association constant at 25 °C reaches 88500 dm³ mol⁻¹, only and thus nearly the value of 96100 reported for LiBr in SO_2 at the same temperature despite the much lower dielectric permittivity of the unidentate ligand solvent methyl formate.

From the temperature dependent association constants quoted in Table 3, thermodynamic data of the ion pair formation process can be simply derived. The Gibbs energy of association, ΔG_A^0 is linked to the association constant K_A by the equation

$$\Delta G_A^0 = -RT \ln K_A \qquad (7)$$

The entropy and enthalpy of the ion pair formation process are obtained with the help of the usual thermodynamic relationships

$$\Delta S_A^0 = -\left(\frac{\partial \Delta G_A^0}{\partial T}\right)_p, \qquad \Delta H_A^0 = \Delta G_A^0 + T\Delta S_A^0 \qquad (8a,b)$$
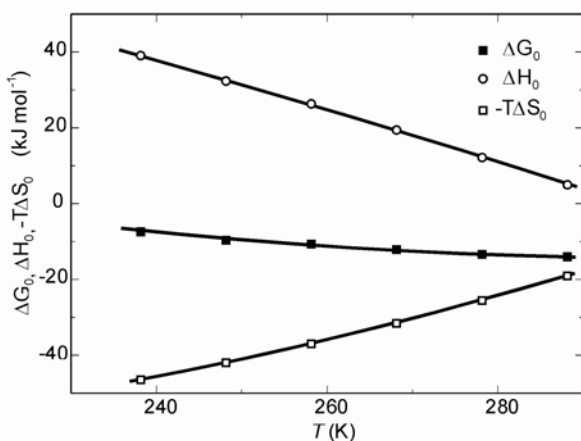

Figure 3. Gibbs energy, enthalpy and entropy for the ion pair formation process.

Figure 3 shows, that the endothermic enthalpy of association ($\Delta H_A^0 > 0$) is compensated by the entropic term to yield negative values for the Gibbs energy of association and therefore favours ion pair formation.

4. Conclusion

The association constant of $LiAlCl_4$ in liquid SO_2 increases by one order of magnitude from 40 to 350 dm³ mol⁻¹ in the temperature range of this investigation (238–288 K). However, compared to other 1.1-salts, $LiAlCl_4$ shows a relatively small association constant. This result is favorable for the use of $LiAlCl_4$ in liquid SO_2 in an inorganic battery based on Li_xC/Li_xCoO_2-electrodes.

5. Acknowledgments

6. References

1 A. Jossen, W. Weydanz, Moderne Akkumulatoren richtig einsetzen, Inge Reichardt Verlag, Untermeitingen, **2006**.

2 H. J. Gores, H.-G. Schweiger, M. Multerer, *Optimizing the conductivity of electrolytes for lithium ion-cells,* in: S. S. Zhang (Ed.) Advanced Materials and Methods for Lithium Ion Batteries, Research Signpost Special Review Books, chapter 11, **2007**.

3 J. O. Besenhard. Handbook of Battery Materials. Wiley-VCH, Weinheim, New York, **1999**.

4 G. Moumouziasa, G. Ritzoulis, D. Siapkas, and D. Terzidis, *J. Power Sources* **2003**, *122*, 57–66.

5 J. Yamaki, in Ref.[7], Chapter. 5, 155.

6 G. E. Blomgren, in Ref.[13], Chapter 2, 52.

7 W. von Schalkwijk, B. Scrosati (Eds.), Advances in Lithium-

Ion Batteries, Kluwer Academic, New York, **2002**.

8 G. A. Nazri, G. Pistoia (Eds.), Lithium Batteries: Science and Technology, Kluwer Academic, New York, **2004**.

9 O. Yamamoto, M. Wakihara, Lithium-Ion Batteries, Wiley-VCH, New York, Weinheim, **1988**.

10 D. Linden, Ed. Handbook of Batteries, McGraw-Hill, 2nd edition, New York, **1995**.

11 K. Nihio, N. Furukawa in Ref.[3], Chapter 2.

12 D. Linden in Ref.[10] Chapter 14.6 .

13 L. A. Dominey, in D. Aurbach (Ed.), Nonaqueous Electrochemistry, Marcel Dekker, New York, Chapter 6, **1999**, p. 437.

14 D. Linden in Ref.[10] Chapter 14.5.

15 D. Linden in Ref.[10] Chapter 14.7.

16 V. Doege, J. Dreher, G. Hambitzer, *Proceedings of the Annual Battery Conference* **1995**, 313–317.

17 J. Dreher, B. Haas, G. Hambitzer, *J. Power Sources* **1993,** *44 (1–3),* 583–587.

18 J. Dreher, B. Haas, G. Hambitzer, *J. Power Sources* **1993,** *44 (1–3 pt. 2),* 583–58

19 L. Zinck, M. Borck, C. Ripp, and G. Hambitzer, *J. Appl. Electrochem.* **2006**, *36(11),* 1291–1295.

20 J. Barthel, H. J. Gores in Ref.[3], Chapter 7, 457.

21 J. Barthel, R. Buchner, H. J. Gores, Struktur der Elektrolytlösung und ionische Leitfähigkeit, DECHEMA Monographien 124, VCH, Weinheim, **1991**, 65.

22 J. Barthel, H. Krienke, W. Kunz, in: H. Baumgärtel (Ed.) Physical Chemistry of Electrolyte Solutions, volume 5. Steinkopff Verlag, Darmstadt, Germany, **1998**.

23 R. Wachter, J. Barthel, *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 634–642.

24 R. R. Wolf. *Leitfähigkeitsmessungen an Lithium- und Tetrabutylammoniumelektrolyten in Butylencarbonat und Acetonitril*. PhD thesis, University of Regensburg, **1996**.

25 J. Barthel, F. Feuerlein, R. Neueder, R. Wachter, *J. Solution Chem* **1980**, *9(3),* 209–219.

26 I. B. Sladkov, M. A. Shmakova, *Russ. J. Appl. Chem* **2007**, *80(3),* 501–503.

27 I. B. Sladkov, *J. Appl. Chem* **2003**, *76(12),* 1909–1913.

28 H. Vogel, *Physik. Z.* **1921**, *22*, 645–646.

29 G. S. Fulcher, *J. Am.Ceram. Soc.* **1925**, *8*, 339–355.

30 G. Tammann, W. Hesse, *Z. Anorg. Allg. Chem.* **1926**, *156*, 245–257.

31 J. H. Awbery, E. Griffiths, *Proc. Phys. Soc* **1936**, *48*, 372–380.

32 J. Barthel, H. Popp, G. Schmeer, *Die ELDAR Methodenbank für Elektrolytlösungen*, in: J. Gasteiger (Ed.): Software-Entwicklung in der Chemie, volume 2. Springer, Berlin, **1988**.

33 A. Simon, K. Peters, E.-M. Peters, *Z. Anorg. Allg. Chem.* **1980**, *469*, 94–100.

34 J. Barthel, R. Wachter, H. J. Gores, *Faraday Discuss. Chem. Soc.* **1977**, *64*, 285–294.

35 J. Barthel, *Pure Appl. Chem.* **1979**, *51*, 2093–2124.

36 S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* **1972**, *77(17),* 2133–2137.

37 K. Fredenhagen, *Z. Anorg. Chem.* **1950**, *261*, 279–282.

38 Y. Marcus, G. Hefter, *Chemical Reviews* **2006**, *106 (11),* 4585–4621.

39 G. B. Nikiforov, C. Knapp, J. Passmore, A. Decken, *J. Fluorine Chem.* **2006**, *127 (10 SPEC. ISS.),* 1398–1404.

40 J. Barthel, H. J. Gores, L. Kraml, *J. Phys. Chem.* **1996**, *100*, 3671.

41 J. Barthel, R. Neueder, in: Gerhard Kreysa (Ed.) Electrolyte Data Collection Vol. 12, Part: 1f, Dechema, Frankfurt am Main (Ger), **2000.**

42 E. Plichta, M. Salomon, S. Slane, M. Uchiyama, *J. Solution Chem.* **1987**, *16(3),* 225.

Povzetek

Izmerili smo električne prevodnosti razredčenih raztopin LiAlCl$_4$ v razredčenih raztopinah žveplovega dioksida v temperaturnem območju med 238.15 K in 288.15 K ter viskoznosti tekočega žveplovega dioksida med 231.46 K in 257.98 K. Dobljene eksperimentalne podatke električne prevodnosti smo analizirali z uporabo kemijskega modela za razredčene raztopine. Dobljene vrednosti konstant asociacije ionov LiAlCl$_4$ v razredčenih raztopinah žveplovega dioksida so presenetljivo nizke: od 42 dm^3 mol^{-1} pri 238.15 K do 354 dm^3 mol^{-1} pri 288.15 K. Ti rezultati kažejo, da so interakcije med molekulami topila in litijevimi ioni močnejše kot pa so interakcije med litijevimi ioni in šibko koordiniranimi tetrakloroaluminatnimi anioni.