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Temperature and concentration effects on the conductivity of LiAlCl₄/SOCl₂ electrolyte solutions

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Abstract

The conductivity of 1.8 M LiAlCl₄/SOCl₂ electrolyte solutions showed the greatest temperature dependence at 298 K. Raman spectra results suggest that the adduct compound is Li(SOCl₂)_{y-x}(SO₂)_x⁺. The structural changes in LiAlCl₄/SOCl₂ electrolyte solutions were analyzed using ⁷Li NMR spectroscopy. The ⁷Li spin-lattice relaxation rate indicated a change in the ionic structure of the electrolyte near 298 K which was confirmed by measuring the chemical shifts and relaxation times under various temperatures and concentrations. The concentration effects on conductivity of LiAlCl₄/SOCl₂ electrolytes were also investigated. All experimental results suggest that the transition phenomenon in LiAlCl₄/SOCl₂ electrolyte solutions is related to the transformation between Li(SOCl₂)_{y-x}(SO₂)_x⁺ and Li(SOCl₂)_y⁺. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Temperature effect; Concentration effect; Conductivity; LiAlCl₄; SOCl₂

1. Introduction

Electrical conductivity in liquids is of great interest to the technological as well as the theoretical scientist. However, limited knowledge about the molecular dynamics of ions in liquids makes it impossible to theorize the factors that determine ionic conductivity in solutions. Physical experiments must be conducted before the relationship between conductivity and relevant factors can be established in order to improve and advance our understanding of the ionic transport mechanism.

The Li/SOCl₂ inorganic electrolyte cell is capable of providing one of the highest energy densities among all practical primary battery systems known to date [1]. The kinetic, thermodynamic, and mechanistic aspects of thionyl chloride reduction have been thoroughly investigated [2–7], but very few studies have addressed the ionic conductivity of electrolyte solutions [8–10]. The goal of this work is to characterize the chemical details of LiAlCl₄/SOCl₂ solutions. Conductivity measurements as well as spectroscopic techniques, such as ⁷Li NMR and Raman, have been used to analyze the systems.

2. Experimental

Thionyl chloride (Merck, GR) was mixed with triphenylphosphite (16 vol.%) and then distilled under argon. The distillate boiling at 78°C was collected. Battery grade LiAlCl₄ (Cerac) was dried at 110°C in a vacuum for 2 h prior to use.

Conductivity measurements were carried out in specially designed cells [11] using a conductivity probe (YSI model 34). All cells were assembled and filled in an argon-filled glove box (VAC model MO40-1). The test cell was thermostated in an ethanol bath with a RL6 Lauda thermostat.

The ⁷Li NMR spectra were conducted on a Bruker MSL-300 spectrometer at a frequency of 116.638 MHz. All the measured samples were sealed in 10 mm NMR tubes. A 5 mm coaxial insert containing lock solvent solution, 0.5 M LiCl in D₂O (99.8%, Merck), was used as the internal reference.

The chemical shifts reported were corrected for differences in bulk diamagnetic susceptibility between samples and references, in accordance with the relationship established by Live and Chan [12] for high field spectrometers. The measurements of spin-lattice relaxation rates (1/T₁) were obtained by using the standard technique of repeated 180°–90° pulse sequences at a resonance frequency of 46.073 MHz for deuterons and 116.638 MHz for ⁷Li nuclei.

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A total of 14 different pulse intervals were used for measuring T_1 and the delay time was maintained at greater than five times T_1 .

Raman spectroscopy experiments were conducted using a Jobin–Yuon U-100 type apparatus. The light sources were a hydrogen ion laser (4765, 4880, and 5145 Å) and a krypton ion laser (6471 and 6764 Å), operating at 200 mV.

3. Results and discussion

Table 1 presents the measured conductivity values of 1.8 M LiAlCl_4 in SOCl_2 electrolyte solutions at various temperatures and, for comparison purposes, data for the 1.8 M $\text{LiAlCl}_4/\text{SO}_2$ system [13]. Both systems show a similar trend. Below 25°C, conductivity increased with increasing temperature, while above 25°C, conductivity decreased with increasing temperature, implying that the chemical nature of the systems change with temperature. Moreover, Table 2 gives the conductivity values of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes at various temperatures and concentrations. It should be noted that maximum conductivity occurred near 2.0 M solutions at all temperatures except below 273 K (or 0°C).

Raman experiments were conducted to examine the structural aspects of the ion-solvent adduct species in the solution and the observed spectra are shown in Fig. 1. The absorption peak which occurred at 1230 cm^{-1} can be attributed to the S–O stretching mode in SOCl_2 [14]. The other peaks observed at lower wave numbers are related to the bonding between lithium ion and SO_2 or SOCl_2

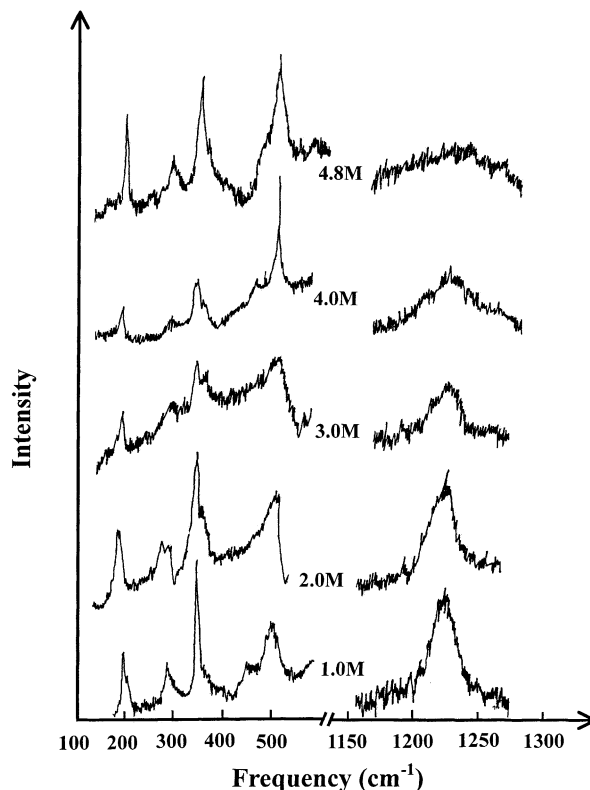


Fig. 1. Raman spectra of the $\text{LiAlCl}_4/\text{SOCl}_2$ system. Concentration of LiAlCl_4 varied from 1.0 to 4.8 M.

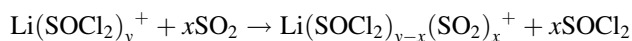
Table 1
Conductivity of 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ and $\text{LiAlCl}_4/\text{SO}_2$ electrolytes at various temperatures

Temperature (K)	Conductivity (m S/cm)	
	$\text{LiAlCl}_4/\text{SOCl}_2$	$\text{LiAlCl}_4/\text{SO}_2$
273	16.0	50.0
278	17.0	51.5
284	18.0	53.0
298	21.0	59.0
308	19.7	55.0
314	19.4	52.5
318	19.1	51.0

Table 2
Conductivity values of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes at various temperatures and concentrations

Temperature (K)	Conductivity (m S/cm)					
	0.1 M	0.5 M	0.8 M	2.0 M	2.5 M	3.0 M
298	2.8	7.5	14.5	19.8	17.6	16.2
273	2.0	7.2	12.8	14.1	14.0	13.0
258	1.9	7.0	12.2	11.8	12.0	11.0
253	1.8	6.6	10.0	9.2	9.7	8.5

molecules [14,15]. It has been shown that the complexes $[\text{Li}(\text{SOCl}_2)_2]^+[\text{AlCl}_4]^-$, $[\text{Li}(\text{SO}_2)_3]^+[\text{AlCl}_4]^-$, and $[\text{Li}(\text{SOCl}_2, \text{SO}_2)]^+[\text{AlCl}_4]^-$ were present at room temperature in pure SOCl_2 , SO_2 , and $\text{LiAlCl}_4\text{-SOCl}_2\text{-SO}_2$ system, respectively [14]. In a neutral electrolyte, the reactive species was $\text{Li}(\text{SOCl}_2)_2^+$ [16,17]. Accordingly, the adduct compound was proposed to be $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$, where y had a maximum value of 2. The mobility and the degree of dissociation (or the $\text{SOCl}_2\text{-SO}_2$ exchange) produced conductivity



At 25°C, $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$ ions formed steadily during cell life. $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$ ions are smaller than $\text{Li}(\text{SOCl}_2)_y^+$ ions and have higher mobility and conductivity. Rising temperature increased mobility, but the degree of dissociation decreased and SO_2 formed which explains why we observed a conductivity maximum and subsequent negative temperature coefficient.

Lithium-7 nuclear magnetic resonance measurements were conducted to determine the structural environment of the lithium ions. Fig. 2 shows a typical plot of the ^7Li spin-lattice relaxation rate ($1/T_1$) of the 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte versus absolute temperature. The two lines, which intersect at a transition point near 298 K, are straight which indicates an Arrhenius behavior while the

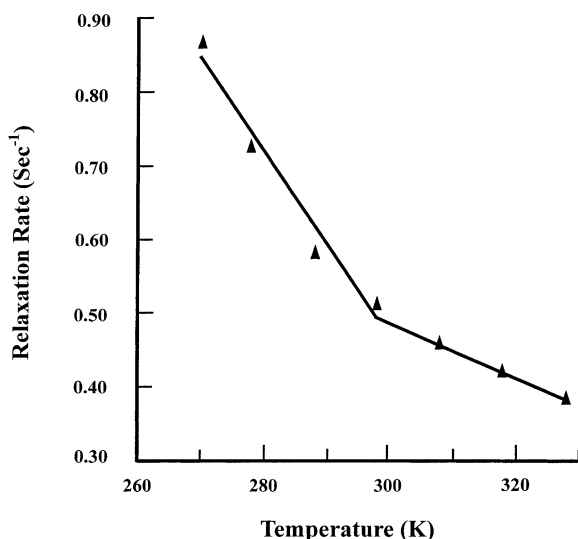


Fig. 2. Lithium-7 spin-lattice relaxation rate of 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte vs. absolute temperature.

change in slope signifies a change in the ionic structure of the electrolyte. These findings support the results of the Raman experiments and conductivity measurements. The activation energies of spin-lattice relaxation for 1.8 M LiAlCl_4 in SOCl_2 above and below 298 K are 7.08 and 12.91 kJ/mol, respectively. The structural changes in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte solutions at 298 K were implied by both ^7Li NMR spectroscopy and conductivity measurements.

Confirmation of the transition which occurs at around 298 K, was further confirmed by measuring the chemical shifts and relaxation times under various temperatures or concentrations, which are shown in Table 3 and Fig. 3, respectively. Fig. 3 indicates that there was a significant change between 298 and 308 K at a concentration near 1.8 M. However, the effects of concentration were greater than the effects of temperature in the dilute solutions of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes and less than the effects of temperature in the concentrated solutions. As shown in Table 3, significant changes in chemical shift were also observed in $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes between 298 and 308 K. It is noteworthy that the non-linear plot in Fig. 3 is indicative of contact-ion-pair formation. The formation

Table 3
Lithium-7 chemical shifts of 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes at various temperatures

Temperature (K)	Chemical shift (ppm)
278	-1.176
288	-1.146
298	-1.116
308	-1.002
318	-0.950
328	-0.900

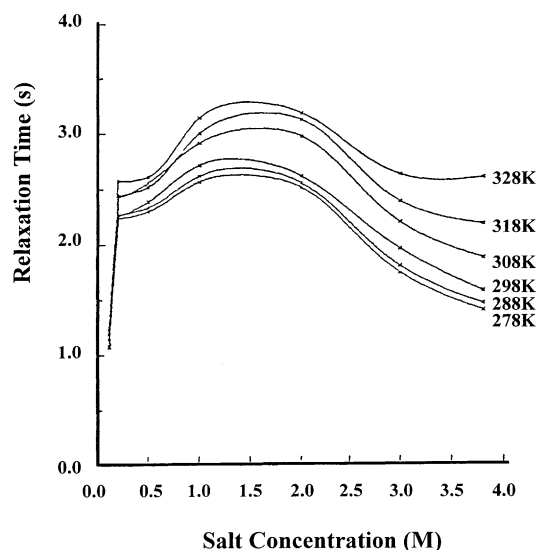


Fig. 3. Concentration effects on relaxation time at various temperatures.

constant of ion pairs in the $\text{LiAlCl}_4/\text{SOCl}_2$ solution can be calculated using Popov's method [18]. The values of ion-pair formation constants are not large, ranging from 10 to 29 M^{-1} , which implies an insignificant presence of ion pairs (e.g. $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+ \cdot \text{AlCl}_4^-$) or inter-ionic association in the temperature range of interest. Conductivity changed with temperature primarily because of the transformation between the solvated ions such as $\text{Li}(\text{SOCl}_2)_y^+$ and $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$.

4. Conclusion

The effects of temperature and concentration on conductivity of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolytes were measured and examined. The most significant finding was the negative temperature coefficient of conductivity when temperatures were above 298 K. A transition point in ionic structure at 298 K was also observed by ^7Li NMR spectroscopy. The activation energies of spin-lattice relaxation for 1.8 M LiAlCl_4 in SOCl_2 above and below 298 K were 7.08 and 12.91 kJ/mol, respectively. Both of NMR and Raman studies suggest that the structure of the adduct species is $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$ and the transformation between $\text{Li}(\text{SOCl}_2)_y^+$ and $\text{Li}(\text{SOCl}_2)_{y-x}(\text{SO}_2)_x^+$ causes the change in conductivity with temperature.

References

- [1] W.H. Behl, J.A. Christopoulos, M. Ramirez, S. Gilman, J. Electrochem. Soc. 120 (1973) 1619.
- [2] W.K. Istone, R.J. Brodd, J. Electrochem. Soc. 131 (1984) 2467.
- [3] F.W. Dampier, T.A. Cole, J. Electrochem. Soc. 133 (1986) 938.
- [4] W.M. Hedges, D. Pletcher, C. Gosden, in: Proceedings of the 32nd International Symposium on Power Sources, Vol. 542, 1986.

- [5] J.G. Chiu, Y.Y. Wang, C.C. Wan, *J. Power Sources* 21 (1987) 119.
- [6] L.D. Hansen, H. Frank, *J. Electrochem. Soc.* 134 (1987) 1.
- [7] Y.K. Choi, B.S. Kim, S.M. Park, *J. Electrochem. Soc.* 140 (1993) 11.
- [8] G.T.K. Fey, *Prog. Batteries Battery Mater.* 12 (1993) 145.
- [9] R.W. Berg, H.A. Hjuler, A.P.L. Sondergaard, N.J. Bjerrum, *J. Electrochem. Soc.* 136 (1989) 323.
- [10] M. Jain, G. Nagasubramanian, R.G. Jungst, J.W. Weidner, *J. Electrochem. Soc.* 146 (1999) 4023.
- [11] G.T.K. Fey, T.J. Lee, C.S. Shiue, L.S. Lin, C.K. Ho, P.C. Yao, Extended Abstract No. 76, The 176th Society Meeting, Hollywood, FL, 15–20 October 1989.
- [12] D.H. Live, S.I. Chan, *Anal. Chem.* 42 (1970) 1791.
- [13] T.J. Lee, Ph.D. Thesis, National Central University, Taiwan, ROC, 1990.
- [14] Y. Bedfer, J. Corset, M.C. Dhamelincourt, F. Wallart, P. Barbier, *J. Power Sources* 9 (1983) 267.
- [15] N.A. Fleischer, M. Pollivathikal, M. Babai, *J. Electrochem. Soc.* 134 (1987) 513.
- [16] P.A. Mosier-Boss, S. Szpak, J.J. Smith, R.J. Nowak, *Electrochim. Acta* 35 (1990) 1787.
- [17] P. Chenebault, in: G. Pistoia (Ed.), *Lithium Batteries: New Materials, Developments and Perspective*, Elsevier, Netherland, 1994, p. 352.
- [18] E.T. Roach, P.R. Handy, A.I. Popov, *Inorg. Nucl. Chem. Lett.* 9 (1973) 359.