Conductivities of Room Temperature Molten Salts Containing $AlCl_3$, Measured by a Computerized Direct Current Method

Hsin-Yi Hsu and Chao-Cheng Yang

Graduate School of Engineering Science & Technology (Doctoral Program), National Yunlin University of Science and Technology, 123 University Road, Sec. 3, Touliu, Yunlin, Taiwan 640, R.O.C.

Reprint requests to Prof. C.-C. Y.; E-mail: yangcc@flame.yuntech.edu.tw; Fax: 886-5-531-2056

Z. Naturforsch. **56a,** 670–676 (2001); received July 23, 2001

The conductivities of the binary room-temperature molten salt systems $AlCl_3$-*N-n*-butylpyridinium chloride (BPC), $AlCl_3$-1-ethyl-3-methylimidazolium chloride (EMIC) and $AlCl_3$-benzyltriethylammonium chloride (BTEAC) have been measured at different temperatures and compositions by a d.c. four-probes method.

There is a maximum of the conductivity at 50 mol% $AlCl_3$ in the $AlCl_3$-BPC and $AlCl_3$-EMIC systems at 40 to 80 °C, their activation energies being relatively low (20.79 and 14.76 kJ/mol, respectively). As to the $AlCl_3$-BTEAC system, there is an irregular change in the conductivity at 40–70 mol% $AlCl_3$ in the temperature range 50 to 80 °C. The conductivities of the three RTMS are in the order $AlCl_3$-EMIC > $AlCl_3$-BPC > $AlCl_3$-BTEAC, the reason being discussed.

Key words: Conductivity; Room-temperature Molten Salts; Activation Energy; Direct Current Method; Computerized Measurement System.

Introduction

Molten salts possess some unique properties, e.g., high conductivity, a wide electrochemical window and low vapor pressure. Therefore they molten salts are suitable electrolytes for the electrodeposition of metals. In recently years, molten salts have extensively been explored for their application as e.g. electrodeposition electrolytes of metals, battery and fuel cell electrolytes, media for plating optical data storage material and melt catalysts for syntheses of new chemicals. Especially research on room temperature molten salts (RTMS) has drawn considerable attention.

Hussey [1] has denoted that industrial exploitation of RTMS looks extremely favorable. Unfortunately, however, conductivity data for RTMS are little known at present.

In the present study, the three systems $AlCl_3$-BPC (*N-n*-butylpyridinium chloride), $AlCl_3$-EMIC (1-ethyl-3-methylimidazolium chloride) and $AlCl_3$-BTEAC (benzyltriethylammonium chloride) were selected for measurements of the conductivities. The conductivity of $AlCl_3$-BPC has been measured by Watanabe et al. [2, 3] with a Horiba conductivity meter DS-7 in a glove box and by Hussey et al. [4] with an a.c. bridge method, while it has not yet been measured with a d.c. four-probes method.

King and Duke [5] have shown that measurement with the usual alternating currents technique of the high specific conductivity of some molten nitrate systems is complicated and demonstrated the practicability of a direct current technique. Duke and Bissell [6] also demonstrated the utility of the d.c. method at the higher temperatures of the KCl-LiCl system. Grantham and Yosim [7] have performed ac and dc conductivity measurements of various Bi-BiI_3 melts and found agreement between them within 0.1%. Therefore, in the present study a computerized measurement system using a d.c. four-probes method processed through a computer program has been employed.

In this work, the conductivities of the systems $AlCl_3$-EMIC and $AlCl_3$-BTEAC are reported for the first time reported. BPC and EMIC are hardly commercially available and therefore expensive, although they are needed as RTMS. BTEAC is commercially available and cheaper. In the present work the conductivities of $AlCl_3$-BPC melts have again been measured, and the results are compared with the data in the literature.

Experimental

$AlCl_3$ (Aldrich, anhydrous, 99.99%). BPC (*N-n*-butylpyridinium chloride, TCI, 98%). EMIC (1-ethyl-3-methylimidazolium chloride, Aldrich, 98%) and BTEAC (benzyltriethylammonium chloride, Acros, 98%) were used as received. The molten salts with different molar ratios were prepared by continuous stirring for 12 hours

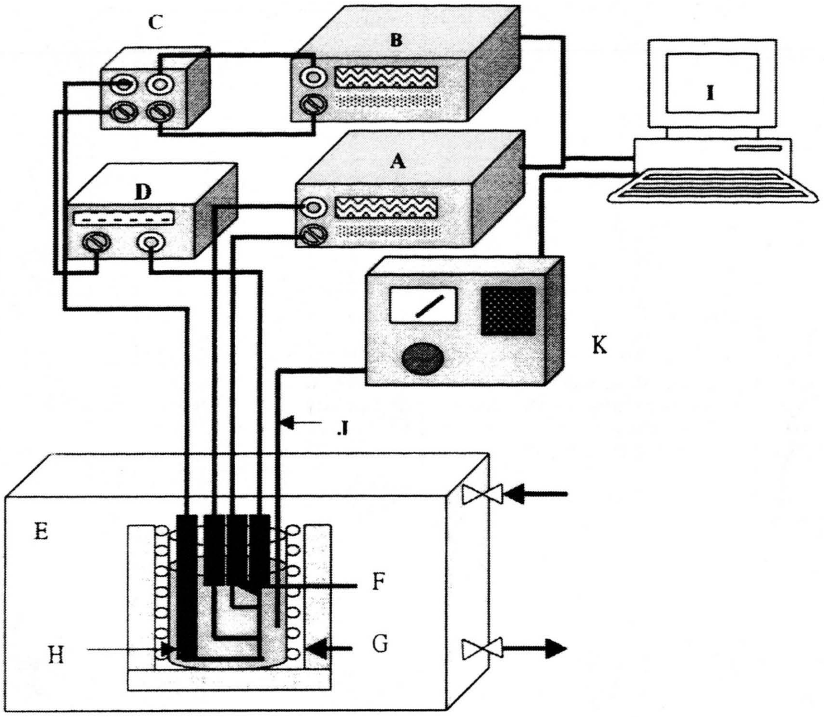

Fig. 1. Apparatus for computerized measurements of the conductivity.
A. Multimeter1
B. Multimeter2
C. 10 Ω standard resistor
D. DC power supply
E. Glove box
F. Conductivity cell
G. Furnace
H. Silicon oil
I. IBM-PC
J. Thermal couple
K. Temperature controller

under a purified nitrogen atmosphere in a glove box. The electric conductivities of these melts were measured by the apparatus shown in Figure 1. The cell (F) was surrounded by silicon oil to improve the temperature homogeneity. The cell constant was determined at 25 °C from the d.c. conductivity of 1 dm KCl prepared according to the specification of Jones and Bradshaw [8]. The thermal expansion of the quartz cell is negligible at the moderate temperatures. Ag-AgCl electrodes and Pt electrodes were used for the measurement of the cell constant, which was found to be 299.8 cm^{-1}.

Pt electrodes were used and the conductivities of the melts were measured under purified nitrogen. The furnace was controlled by a PID-controller, the thermocouple of which measured the temperature in the silicon oil bath. The temperature of the melt near the voltage drop section was also measured by a thermocouple.

The computerized measurement system for the d.c. four-probes method consisted of a personal computer, two multimeters (Keithley, Model 2000), a d.c. power supplier and a standard 10 Ω resistance. The control program was edited from the test point soft program (Keithley). A personal computer was used to control the measuring device, to record the data and to evaluate the conductivities of the melts.

Results and Discussion

The relationships between the conductivity and the temperature of the binary $AlCl_3$-BPC, $AlCl_3$-EMIC and $AlCl_3$-BTEAC melt systems are shown in Figs. 2, 3 and 4, respectively. The experimental date were least-squares fitted to equations of the form $\kappa = a + bt + ct^2$, where t is the temperature in °C. The obtained parameters a, b, and c are given in Tables 1, 2 and 3. As the R squared values are larger than 0.998, the above equations fit the experimental data very well. Figs. 2 and 3 show that the specific conductivities of the $AlCl_3$-BPC and $AlCl_3$-EMIC systems increase nearly linearly with the temperature, which is not the case for the $AlCl_3$-BTEAC system (Figure 4).

These conductivities were fitted by the Arrhenius equation [9–12]

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right). \quad (1)$$

Plots of the data for the $AlCl_3$-BPC, $AlCl_3$-EMIC and $AlCl_3$-BTEAC melts are shown in Figs. 5, 6 and 12, respectively. These results reveal that these data obey the Arrhenius equation over the temperature range studied. The found activation energies (E_a) are presented in Ta-

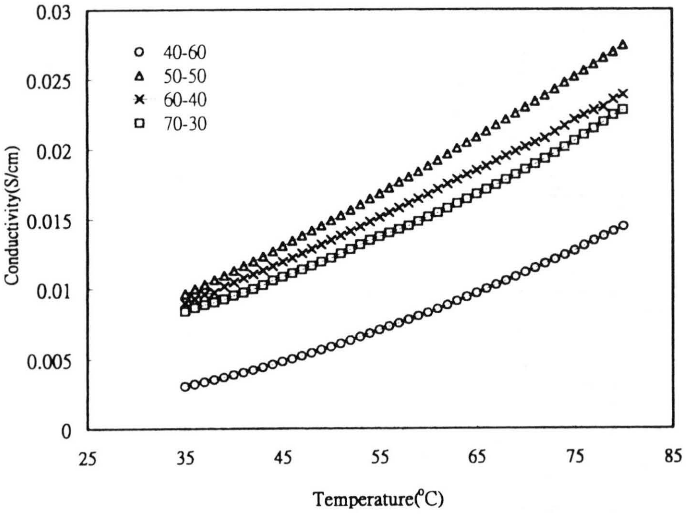

Fig. 2. The electrical conductivity of molten mixtures of $AlCl_3$:BPC as a function of temperature. Composition in mol%: ○, 40:60; △, 50:50; ×, 60:40; □, 70:30.

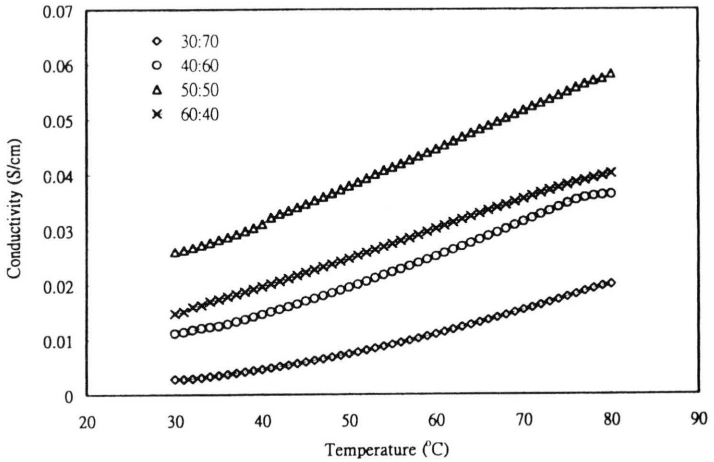

Fig. 3. The electrical conductivity of molten mixtures of $AlCl_3$:EMIC as a function of temperature. Composition in mole%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

Table 1. Parameters for the electrical conductivity equation of $AlCl_3$-BPC.

Melt composition	$a\times10^{-3}$	$b\times10^{-4}$	$c\times10^{-6}$	R squared	Temp. °C
40 mole% $AlCl_3$	14.097	0.76966	2.1375	0.99998	35–80
50 mole% $AlCl_3$	–33.410	23.47871	1.4041	0.99998	35–80
60 mole% $AlCl_3$	9.359	21.98310	0.9665	0.99980	35–80
70 mole% $AlCl_3$	408.312	4.22539	2.3712	0.99950	35–80

Table 2. Parameters for the electrical conductivity equation of $AlCl_3$-EMIC.

Melt composition	$a\times10^{-3}$	$b\times10^{-4}$	$c\times10^{-6}$	R squared	Temp. °C
30 mole% $AlCl_3$	95.79	59.10	3.8	0.99983	30–80
40 mole% $AlCl_3$	1.540	2.116	3.0	0.99837	30–80
50 mole% $AlCl_3$	7.429	5.680	1.0	0.99949	30–80
60 mole% $AlCl_3$	37.85	4.927	27.0	0.99942	30–80

Table 3. Parameters for the electrical conductivity equation of $AlCl_3$-BTEAC.

Melt composition	$a\times10^{-3}$	$b\times10^{-4}$	$c\times10^{-6}$	R squared	Temp. °C
40 mole% $AlCl_3$	3.4973	1.252	1.3	0.99996	60–130
50 mole% $AlCl_3$	2.173	9.5	1.0	0.99999	50–130
60 mole% $AlCl_3$	2.7207	1.036	1.207	0.99998	50–130
70 mole% $AlCl_3$	48.8	26.2	80.0	0.99993	30–80

Table 4. Activation energies (E_a) from Arrhenius fits of the conductivity data.

Melt composition	$E_a\sigma$ (kJ/mol)				
	30:70	40:60	50:50	60:40	70:30
$AlCl_3$-BPC		30.97	20.79	19.40	19.86
$AlCl_3$-EMIC	36.12	22.29	14.76	17.76	
$AlCl_3$-BTEAC		44.82	38.69	39.81	37.82

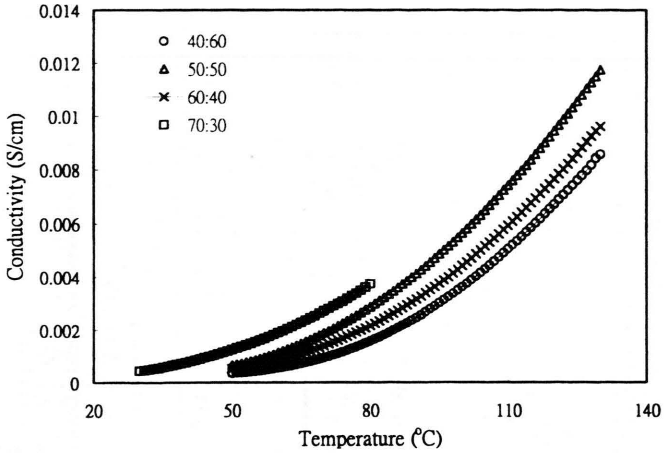

Fig. 4. The electrical conductivity of molten mixtures of $AlCl_3$:BTEAC as a function of temperature. Composition in mol%: ○, 40:60; △, 50:50; ×, 60:40; □, 70:30.

ble 4 [11, 12], which indicates that the binary $AlCl_3$-EMIC melts have the lowest conductivity activation energy among these mixtures. The results may be explained in terms of the degree of planarity and the scale of lattice energy [13, 14]. The planarity inherent mostly in the imidazolium salt is assumed to promote the conductivity. Further, the lattice energy of $AlCl_3$-EMIC melts is considered to be the lowest. In contrast, the binary $AlCl_3$-BTEAC melts have the highest activation energy, presumably because of the poor planarity and higher lattice energy, resulting in the low conductivity. Generally, a salt with a low lattice energy tends to show a high ionic conductivity, because a low dissociation energy increases the number of free ions.

The relationships between conductivity and composition of the systems $AlCl_3$-BPC, $AlCl_3$-EMIC and $AlCl_3$-BTEAC at various temperatures are shown in Figs. 7, 8 and 9, respectively. Figure 7 shows that there is a maximum of the conductivity at 50 mol% $AlCl_3$ for temperatures from 40 to 80 °C. In the system $AlCl_3$-BPC, the following acid-base equilibria are generally supposed [15–22]:

$$BP^+Cl^- + AlCl_3 \Leftrightarrow BP^+ + AlCl_4^- \quad : K_1, \qquad (2)$$

$$AlCl_4^- + AlCl_3 \Leftrightarrow + Al_2Cl_7^- \quad : K_2, \qquad (3)$$

$$2AlCl_4^- \Leftrightarrow Al_2Cl_7^- + Cl^- \quad : K_3, \qquad (4)$$

where $K_1 - K_3$ are the equilibrium constants and K_3 is much smaller than K_1 and K_2. In this system, BP^+ is the only cationic species, and the anionic species vary with the compositions. At $AlCl_3$/BPC = 1 (neutral melt), $AlCl_4^-$ is the only existing anionic species. At $AlCl_3$/BPC > 1 (acidic melts), $Al_2Cl_7^-$ is formed because the reaction (3) proceeds toward the right-hand side. At $AlCl_3$/BPC < 1 (basic melts), Cl^- is left in addition to the formation of $AlCl_4^-$. The decrease of the conductivity in the basic melts has been attributed to the increase in the viscosity with decreasing $AlCl_3$. On the other hand, the conductivity decrease in the acidic melts has been attributed to the formation of larger anions like $Al_2Cl_7^-$. The slope of conductivity decrease in the acidic melts is less sharp than that in the basic melts, because the viscosity decrease with increasing $Al_2Cl_7^-$ is partly compensated by the $AlCl_4^-$ produced by the decomposition of $Al_2Cl_7^-$. The conductivities of $AlCl_3$-BPC melts agree well with the data of previous work [2, 3], which demonstrates the practicability and preciseness of the present computerized measurement system.

Figure 8 shows that the conductivity is maximum at 50 mol% $AlCl_3$ and 30 to 80 °C. In the $AlCl_3$-EMIC melt system, the acid-base equilibria of ionic reactions may be similar to those in the $AlCl_3$-BPC melt [22, 23].

Figure 9 shows that there is an irregular change at 40–70 mol% $AlCl_3$ and 50–80 °C. BTEAC is an asymmetric aliphatic compound which may result in the irregular behaviour.

BPC and EMIC have aromatic cations of pyridinium and imidazolium, respectively. BTEAC has an aliphatic onium cation. Figure 10 shows the electrical conductivity of the melts $AlCl_3$-BPC, $AlCl_3$-EMIC and $AlCl_3$-BTEAC with 50% $AlCl_3$ as a function of temperature. The $AlCl_3$-EMIC melt has the largest slope of the conductivity as a function of temperature and clearly a higher conductivity than the other two melts. The results may be explained in terms of the planarity and lower lattice energy.

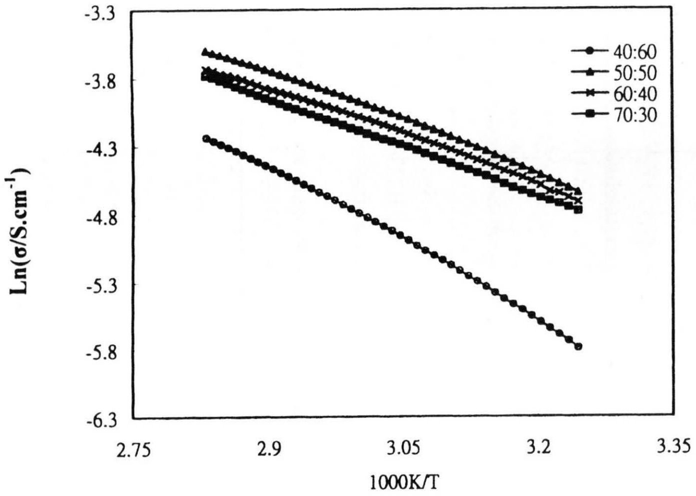

Fig. 5. Arrhenius plots of the electrical conductivity for molten mixtures of $AlCl_3$:BPC. Composition in mol%: ○, 40:60; △, 50:50; ×, 60:40; □, 70:30.

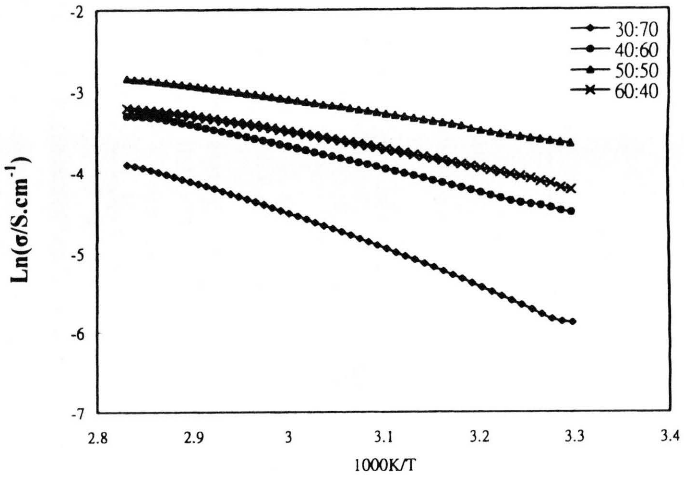

Fig. 6. Arrhenius plots of the electrical conductivity for molten mixtures of $AlCl_3$:EMIC. Composition in mol%: ◇, 30:70; ○, 40:60; △, 50:50; ×, 60:40.

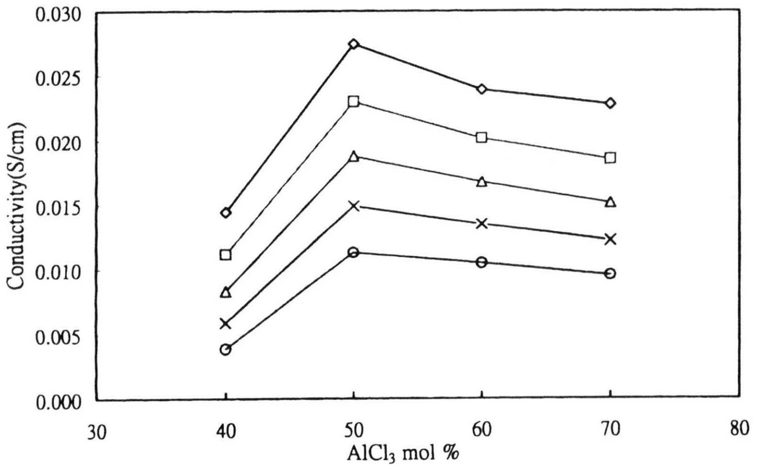

Fig. 7. The electrical conductivity of molten $AlCl_3$-BPC as a function of the mol% of $AlCl_3$ at different temperatures. ◇, 80 °C; □, 70 °C; △, 60 °C; ×, 50 °C; ○, 40 °C.

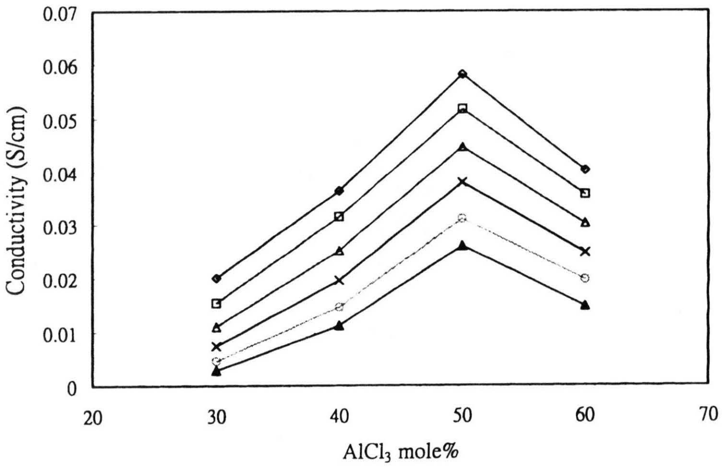

Fig. 8. The electrical conductivity of molten $AlCl_3$-EMIC as a function of the mol% of $AlCl_3$ at different temperatures. ◇, 80 °C; □, 70 °C; △, 60 °C; ×, 50 °C; ○, 40 °C; ▲, 30 °C.

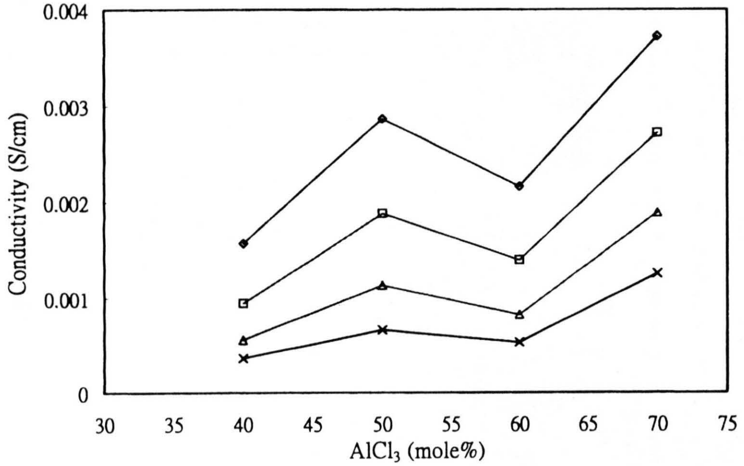

Fig. 9. The electrical conductivity of molten $AlCl_3$-BETAC as a function of the mol% of $AlCl_3$ at different temperatures. ◇, 80 °C; □, 70 °C; △, 60 °C; ×, 50 °C.

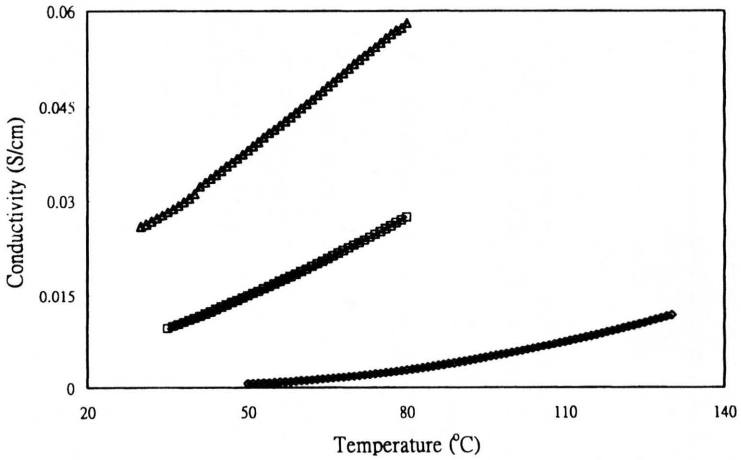

Fig. 10. Temperature dependence of the electrical conductivity of the three binary molten mixtures with 50 mol% $AlCl_3$. ■, $AlCl_3$-BPC; ▲, $AlCl_3$-EMIC; ◆, $AlCl_3$-BTEAC.

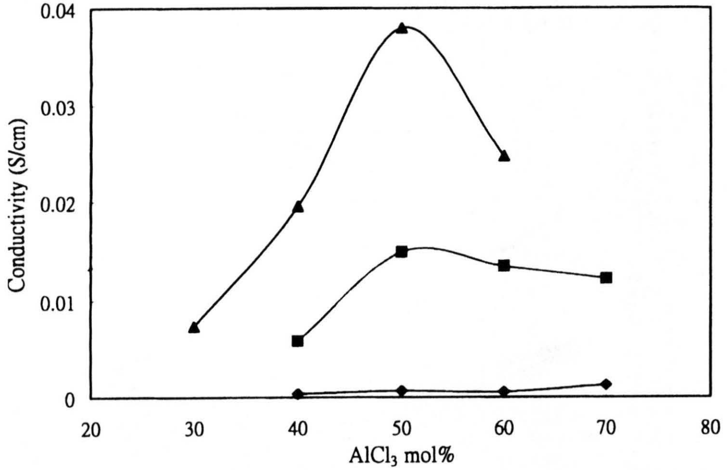

Fig. 11. The electrical conductivity of the three molten mixtures as a function of the $AlCl_3$ mol% at 50 °C. ■, $AlCl_3$-BPC; ▲, $AlCl_3$-EMIC; ◆, $AlCl_3$-BTEAC.

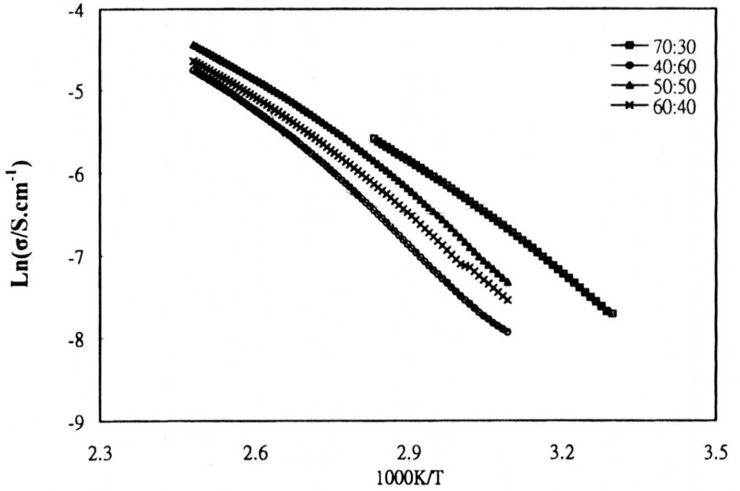

Fig. 12. Arrhenius plots of the electrical conductivity for molten mixtures of $AlCl_3$:BTEAC. Composition in mol%: ○, 40:60; △, 50:50; ×, 60:40; □, 70:30.

Figure 11 shows the electrical conductivity of the three binary melts as a function of composition at 50 °C. The $AlCl_3$-EMIC melt system shows a remarkable change as a function of the composition. As to the conductivities $AlCl_3$-EMIC > $AlCl_3$-BPC > $AlCl_3$-BTEAC.

Conclusions

In the $AlCl_3$-BPC and $AlCl_3$-EMIC melts there is a maximum of the conductivity at 50 mol% $AlCl_3$. Furthermore, the activation energies at 50 mol% $AlCl_3$ melts are relatively low: 20.79 and 14.76 kJ/mol, respectively. On the other hand, in the $AlCl_3$-BTEAC melt there is an irregular change of the conductivity between 40 and 70 mol% $AlCl_3$ in the temperature range from 50 to 80 °C.

The sequence of conductivity for the three binary melt systems is $AlCl_3$-EMIC > $AlCl_3$-BPC > $AlCl_3$-BTEAC.

Acknowledgement

We are indebted to Professor Isao Okada for advise.

[1] C. L. Hussey, Electrochemistry **67,** 527 (1999).
[2] M. Watanabe, S.-I. Yamada, and N. Ogata, Electrochim. Acta **40,** 2285 (1995).
[3] N. Ogata, K. Sanui, M. Rikukawa, S. Yamada, and M. Watanabe, Synth. Met. **69,** 521 (1995).
[4] R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi, and C. L. Hussey, J. Electrochem. Soc. **126,** 1644 (1979).
[5] L. A. King and F. R. Duke. J. Electrochem. Soc. **111,** 712 (1964).
[6] F. R. Duke and L. Bissell, J. Electrochem. Soc. **111,** 717 (1964).
[7] L. F. Grantham and S. J. Yosim. J. Chem. Phys. **38,** 1671 (1963).
[8] G. J. Janz and R. P. T. Tomkins, J. Electrochem. Soc. **124,** 55c (1977).
[9] R. A. Carpio, L. A. King, F. C. Kibler, Jr., and A. A. Fannin, Jr., J. Electrochem. Soc. **126,** 1650 (1979).
[10] K. Ito, N. Nishina, and H. Ohno, Electrochim. Acta **45,** 1295 (2000).
[11] J. D. Edwards, C. S. Taylor, A. S. Russell, and L. F. Maranville, J. Electrochem. Soc. **90,** 527 (1952).
[12] H. Every, A. G. Bishop, M. Forsyth, and D. R. MacFarlane, Electrochim. Acta **45,** 1279 (2000).
[13] M. Hirao, K. Ito, and H. Ohno, Electrochim. Acta **45,** 1291 (2000).
[14] D. R. McFarlane, J. Sun. J. Golding, P. Meakin, and M. Forsyth, Electrochim. Acta **45,** 1271 (2000).
[15] R. A. Osteryoung, in "Molten Salt Chemistry", Eds. G. Mamantov and R. Marassi, D. Reidel Pub., Dordrecht, Amsterdam 1987, pp 329–364.
[16] R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem. **17,** 2728 (1978).
[17] R. J. Gale and R. A. Osteryoung, Inorg. Chem. **18,** 1603 (1979).
[18] Z. J. Karpinski and R. A. Osteryoung, Inorg. Chem. **23,** 1491 (1984).
[19] L. Heerman and D'Olieslager, Inorg. Chem. **24,** 4704 (1985).
[20] J. Robinson, R. C. Bugle, H. L. Chum, D. Koran, and R. A. Osteryoung, J. Amer. Chem. Soc. **101,** 3776 (1979).
[21] J. P. Schoebrechts and B. P. Gilbert, J. Electrochem. Soc. **128,** 2679 (1981).
[22] Z. J. Karpinski and R. A. Osteryoung, Inorg. Chem. **24,** 2259 (1985).
[23] J. S. Wilkes, J. S. Frye, and G. F. Reynolds, Inorg. Chem. **22,** 3870 (1983).