The Electrical Conductivity and Activation Energy for Ionic Conductance of the Fused Salts Mixtures

By

Yoshitaka Matsumura*, Masao Mizuno* and Kiyokado Nishihara**

The electrical conductivity of the fused salt systems KCl-LiCl, KCl-NaCl, KCl-KBr and NaCl-NaBr have been determined as functions of both temperature and molar fractions, and the activation energy for ionic conductance is calculated with Frenkel's theory.

The isotherms of equivalent conductivity against molar fractions for system KCl-LiCl showed negative deviation from additivity and a minimum value was found at 20 mol % LiCl. The activation energy showed positive deviation from additivity and a maximum value was found at 40 mol % LiCl.

In the KCl-NaCl, KCl-KBr and NaCl-NaBr systems, the isotherms of equivalent conductivity showed negative deviation from additivity and the activation energy showed positive deviation.

The deviation of the activation energy from additivity are caused by the interactions between different types of cation and cation hole or anion and anion hole in the liquid mixture.

1. Introduction

The electrical conductivity of the fused salts mixture has been investigated by B. Poincare[1], E. Heymann and I. S. Yaffe[2] and others[3], both from the theoretical viewpoint of wishing to gain a clearer insight into the behavior of liquid mixtures and from the practical standpoint of wanting to be able to predict the electrical conductivity of a fused salts mixture from the properties of the pure components.

A number of prior publications have pointed out that various maxima, minima and other points of inflection can be found in electrical conductivity isotherms for fused salts mixtures. Such points of inflection have frequently been considered to indicate the existence of complex ion in melts. In the alkali halide fused mixture, nevertheless there is no evidence for the formation of complex ion in melts, the isotherms of conductivity show negative or positive deviation from additivity.

We investigated the electrical conductivity of fused KCl-LiCl, KCl-NaCl,

---

* Department of Metal Science and Technology.
** Department of metallurgy

KCl-KBr and NaCl-NaBr systems.

The isotherms of electrical conductivity against molar composition were determined over extended temperature ranges for these systems and the activation energy for ionic conductance was calculated.

2. Activation energy for ionic conductance of fused salt

The fused slat may be treated as a very disorderd solid, making use of concepts due to Frenkel[5], Schottky, Jost and others. These investigators have related diffusion and ionic conductance in solid salts with irreversible and reversible imperfection of the crystal lattice. The high temperature, i.e. structure-insensitive, conductivity of ionic crystal is proportional to the number of lattice defect per c.c. and to their mobility. Both factors vary exponentially with temperature and an expression

$$\kappa = A \exp\left\{-(1/2 \cdot W + U)/kT\right\} \tag{1}$$

is obtained, where W is the energy necessary to produce the lattice defect and U is the height of the energy barrier involved in its migration.

In the fused salt, the lattice is presumably disorderd to such an extent that the fraction of mobile ions may be assumed to be very great and within certain limits, virtually independent of temperature, provided no constitutional changes take place with a change of temperature.

The contribution of each ionic species to the conductivity will be proportional to an exponential term containing only the U-term of equation (1). For purely ionic binary melt, a relation of the form

$$\kappa = A \exp\left\{-E_\kappa/RT\right\} \quad \text{or} \quad \varLambda = B \exp\left\{-E_\varLambda/RT\right\} \tag{2}$$

may be expected, where $E_\varLambda$ may be called the activation energy for ionic conductance, and $E_\varLambda$ was assumed as follows, with the meaning of the quasi-chemical reaction approach[6],

N_A : number of anions per mole in the melt

N_C : number of cations per mole in the melt

a　: number of ion pairs in the melt

n_A : number of anion holes per mol in the melt

n_C : number of cation holes per mol in the melt

α　: number of coupled vacancies per mol in the melt

D_A : diffusion coefficient of anion

D_C : diffusion coefficient of cation

Z　: coordination number

H_A : jumping energy of anion into an anion hole

H_C : jumping energy of cation into a cation hole

H_A' : jumping energy of anion into a coupled vacancy

H_C' : jumping energy of cation into a coupled vacancy

$$E = Z/2 \left[\{D_C/(D_C+D_A)\} \{(N_C-a)(n_C-\alpha) \cdot H_C+(N_C-a) \cdot \alpha \cdot H_C'\} \right.$$
$$\left. + \{D_A/(D_C+D_A)\} \{(N_A-a)(n_A-\alpha) H_A+(N_A-a) \cdot \alpha \cdot H_A'\} \right] \quad (3)$$

Two additional assumptions are made at this point

$$H_C = H_C' \quad \text{and} \quad H_A = H_A'$$

From these assumptions equation (3) can be written as follows

$$E = Z/2 \left[\{D_C/(D_C+D_A)\} \cdot (N_C-a) \cdot n_C \cdot H_C + \{D_A/(D_C+D_A)\} (N_A-a) \cdot n_A \cdot H_A \right]$$
$$(4)$$

3. Apparatus and Experimental Procedure

The electrical conductivity was measured by means of a Wheatstone bridge circuit using a Kohlrausch type. The measurements were made at a frequency of 800 cyc./sec.. The conductivity cell used in the investigation is illustratetd in Fig. 1. The cell was a simple U-tube alumina capillary. The point of balance detected by a magic eye.

The cell constant of U-tube was determined with pure KCl at temperatures $790 \sim 900°C$.

We measured the electrical resistance of the fused salts mixture and calculated the specific conductivity by the following equation,

$$R = C/\kappa_t$$

    R : electrical resistance

    κ_t : specific conductivity of the fused salt at $t°C$,

    C : cell constant at $t°C$,

The equivalent conductivity of fused salt mixtures was calculated by following equation,

$$\Lambda_m = (\kappa_t+E_m)/d,$$

    d : density of the fused salts mixture

    E_m : mean equivalent weight

    $$E_m=E_1 f_1+E_2 f_2$$

        E_1, E_2 : equivalent weight

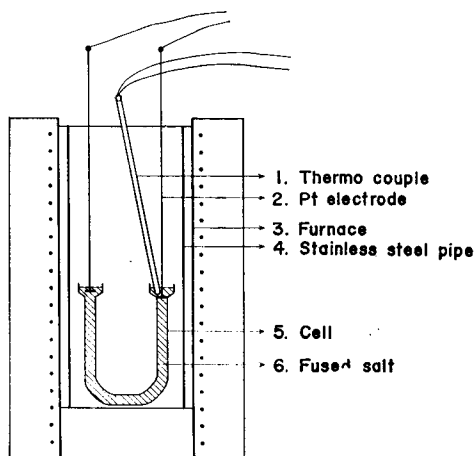 f_1, f_2 : equivalent fraction of component 1 and 2,

Fig. 1.   Apparatus for determination of electrical
conductivity.

4.   Results

The specific conductivity of fused KCl-LiCl, KCl-NaCl, KCl-KBr and NaCl-NaBr systems were measured at temperatures 600~900°C, and the equivalent conductivity was calculated from the specific conductance and the equivalent volume.

The variation in specific conductivity with both temeprature and molar composition for the systems KCl-LiCl, KCl-NaCl, KCl-KBr and NaCl-NaBr are shown in table 1,2,3 and 4.   The isotherms of equivalent conductivity of these systems plotted against molar fraction of KCl or NaCl in the fused salts mixtures are shown in Fig. 2,3,4 and 5, together with the activation energy for ionic conductance.

4.1   KCl-LiCl and KCl-NaCl systems

The isotherms of equivalent conductivity of KCl-LiCl system showed negative deviation from additivity and a minimum value was found at 20 mol% LiCl. The activation energy for ionic conductance shows positive deviation from additivity and a maximum value was found at 40 mol% LiCl.   The degree of positive deviation of activation energy from additivity at each composition corresponds to the degree of negative deviation of equivalent conductivity, and at 50 mol% LiCl, both deviations show maximum value.

In KCl-NaCl system, the isotherms of equivalent conductivity show negative deviation from additivity and it increases with increasing the NaCl content in the mixture, the activation energy shows positive deviation but the degree of deviation from additivity was smaller than that of KCl-LiCl system.

Table 1.   Specific conductivity and Activation energy for ionic conductance in KCl-LiCl system.

Composition (mol%)		Temperature (°C)	Specific conductivity (ohm^{-1}·cm^{-1})	Activation energy (Kcal/mol)
KCl	LiCl			
100	0	800	2.24	
100	0	840	2.33	3.32
100	0	880	2.43	
80	20	700	2.07	
80	20	750	2.24	3.84
80	20	800	2.40	
60	40	600	1.86	
60	40	650	2.09	3.68
60	40	700	2.33	
41	59	550	2.13	
41	59	600	2.40	3.70
41	59	650	2.67	
18	82	600	3.64	
18	82	650	3.70	2.78
18	82	700	3.95	
0	100	700	6.24	
0	100	750	6.38	1.56
0	100	800	6.53	

Table 2.   Specific conductivity and Activation energy for ionic conductance in KCl-NaCl system.

Composition (mol%)		Temperature (°C)	Specific conductivity (ohm^{-1}·cm^{-1})	Activation energy (Kcal/mol)
KCl	NaCl			
80	20	800	2.35	
80	20	840	2.45	3.40
80	20	880	2.52	
60	40	760	2.39	
60	40	800	2.50	3.43
60	40	840	2.61	
40	60	760	2.67	
40	60	800	2.78	3.24
40	60	840	2.88	
20	80	760	2.93	
20	80	800	3.05	3.00
20	80	840	3.16	
0	100	840	3.64	2.67
0	100	880	3.74	

Table 3. Specific conductivity and Activation energy for ionic conductance in KCl-KBr system.

| Composition (mol%) | | Temperature (°C) | Specific conductivity (ohm^{-1}·cm^{-1}) | Activation enerfiy (Kcal/mol) |
KCl	LiCl			
100	0	813	2.27	
100	0	853	2.37	3.32
100	0	893	2.45	
80	20	813	2.16	
80	20	853	2.24	3.29
80	20	893	2.32	
60	40	813	2.02	
60	40	853	2.12	3.36
60	40	893	2.20	
40	60	813	1.95	
40	60	853	2.02	3.31
40	60	893	2.10	
20	80	813	1.85	
20	80	853	1.93	3.50
20	80	893	2.01	
0	100	183	1.78	
0	100	853	1.86	3.86
0	100	893	1.92	

Table 4. Specific conductivity and Activation enerfiy for ionic conductance in NaCl-NaBr system.

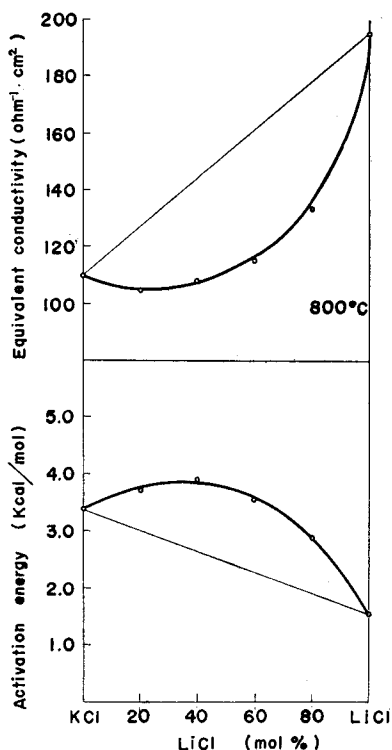| Composition (mol%) | | Temperature (°C) | Specific conductivity (ohm^{-1}·cm^{-1}) | Activation enerfiy (Kcal/mol) |
NaCl	NaBr			
100	0	833	3.63	
100	0	853	3.69	2.83
100	0	893	3.79	
80	20	833	3.46	
80	20	853	3.52	2.89
80	20	893	3.63	
60	40	833	3.33	
60	40	853	3.38	2.86
60	40	893	3.49	
40	60	833	3.18	
40	60	853	3.23	2.84
40	60	893	3.33	
20	80	833	3.07	
20	80	853	3.14	2.90
20	80	893	3.23	
0	100	833	3.01	
0	100	853	3.05	2.86
0	100	893	3.09	

Fig. 2. Electrical conductivity and activation energy in KCl-LiCl system.
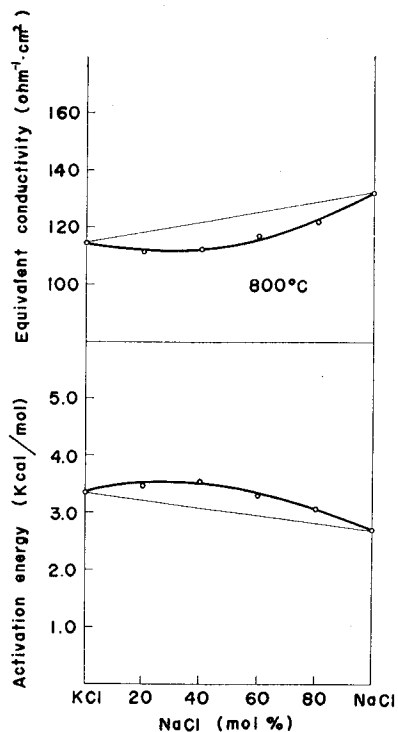

Fig. 3. Electrical conductivity and activation energy in KCl-NaCl system.

4.2 KCl-KBr and NaCl-NaBr systems

The isotherms of equivalent conductivity of KCl-KBr system showed negative deviation from additivity, but the degree of deviation from additivity was smaller than that of KCl-NaCl system, and it decreases with increasing the KBr content in the liquid mixture. The activation energy for ionic conductance shows negative deviation from additivity.

In NaCl-NaBr system, the isotherms of equivalent conductivity of this system showed negative deviation from additivity and it decreases slightly with increasing the NaBr content in the mixture. The activation energy is almost linear in all compositions.

5. Discussion

The phase diagram of KCl-LiCl system indicates a simple eutectic with no solid solution and KCl-NaCl system forms mixed crystals as well as a eutectic[7]. There is no evidence[8] for the formation of complex ion in the melts, and the molar volume of these mixtures indicate a good agreement with the additivity of molar
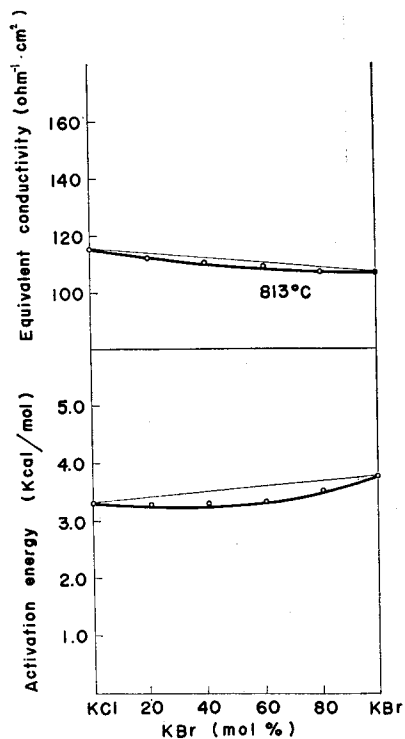
Fig. 4.   Electrical conductivity and activa-
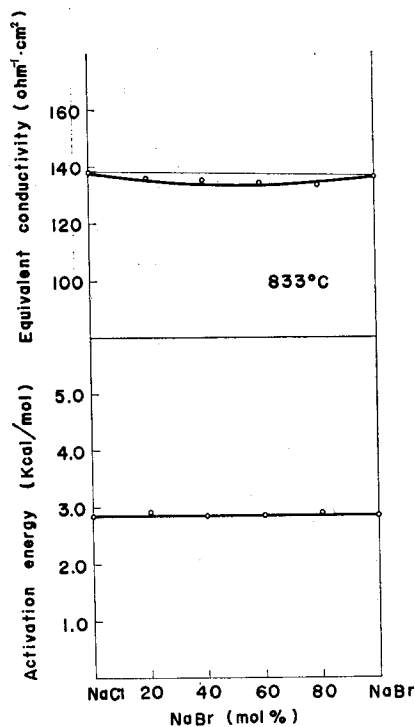tion energy in KCl-KBr system.

Fig. 5.   Electrical conductivity and activa-
tion nergy in NaCl-NaBr system.

compositions within 2%.   Then we consider that the deviation of activation energy for ionic conductance from additivity are caused by some interaction between different types of ions in the liquid mixture.

In the KCl-LiCl and KCl-NaCl systems, the degree of deviation of activation energy from additivity corresponds to the ratio of the ionic radius of K^+ ion to the ionic radius of Li^+ ion or Na^+ ion, i.e. r_{K^+}/r_{Li^+}, r_{K^+}/r_{Na^+}.   Consequently, we consider that the activation energy for ionic conductance of fused salts mixture is affected by some interaction between K^+ ion and Li^+ ion or Na^+ ion; in these systems, when a K^+ ion migrates into the nearest cation hole, there are two cases, 1: a K^+ ion migrates into a K^+ ion hole, 2: a K^+ ion migrates into a Li^+ ion hole.

The type of interaction with cation and cation's hole in the KCl-LiCl system is shown in Fig. 6.   The type of interaction shown in Fig. 6(a) would correspond to the activation energy of pure KCl, the interaction 6(d) would correspond to the activation energy of pure LiCl, the interaction of type 6(b) would correspond to K^+ ion and Li^+ ion hole and the activation energy will be referred as E_{AB}, the interaction of type 6(c) would correspond to Li^+ ion and K^+ ion hole and the activation
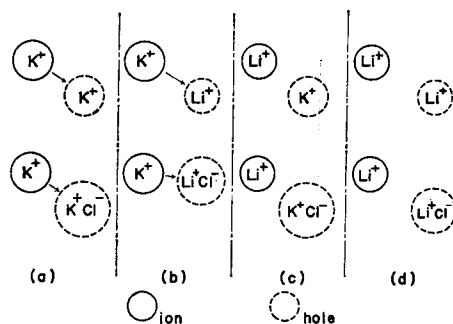
Fig. 6. The type of interaction and hole in a
binary mixture (KCl-LiCl system).

energy will be referred as E_{BA}.

In any binary mixture of mol fraction x_1 the fraction of type (a) in total occurrences would be $x_1{}^2$, as long as the number of cations of type A and B are distributed at random in the liquid mixture.

Corresponding occurrences of the various type of interaction are listed in table 5;

Table 5. Type of interaction and its fraction of total occurrence.

Type of interaction	(a) in Fig. 5	(b) in „	(c) in „ .	(d) in „
Fraction of total occurrences	$x_1{}^2$	$x_1 x_2$	$x_1 x_2$	$x_2{}^2$
Activation energy	E_A	E_{AB}	E_{BA}	E_B

x_1 : mol fraction of KCl in the systems KCl-LiCl, KCl-NaCl and KCl-KBr. mol fraction of NaCl in NaCl-NaBr system.

x_2 : mol fraction of LiCl, NaCl or KBr in the systems KCl-LiCl, KCl-NaCl and KCl-KBr. mol fraction of NaBr in NaCl-NaBr system.

The assumption made here of course is .that probability for the interaction is dependent only on the concentration and not on the activation energy for ionic conductance.

It may be assumed that an activation energy in the mixture may be shown as follows;

$$E_M = x_1{}^2 E_A + x_1 x_2 E_{AB} + x_1 x_2 E_{BA} + x_2{}^2 E_B \qquad (7)$$

An additional assumption is made at this point;

$$E_{\dot{A}} = (E_{AB} + E_{AB})/2$$

From this assumption equation (7) can be written as;

$$E_M = x_1^2 E_A + 2x_1 x_2 E_{\dot{A}} + x_2^2 E_B$$
$$= x_1 E_A + x_2 E_B + 2x_1 x_2 \{E_{\dot{A}} - 1/2 \cdot (E_A + E_B)\} \qquad (8)$$
$$2x_1 x_2 \{E_{\dot{A}} - 1/2 \cdot (E_A + E_B)\} : \text{ excess energy of mixing}$$

In KCl-KBr and NaCl-NaBr systems, we consider that the deviation of activation energy from additivity is caused by the interaction with Cl^- ion and Br^- ion hole or Br^- ion and Cl^- ion hole, and the type of interaction and its occurrences are same as shown in table 5.

We calculated the activation energy for ionic conductance in these systems with equation (8) and with equation (2) using experimental data.

The results are shown in table 6 and 7.

It can easily be seen that the values calculated with equation (8) are all in close agreement with those calculated with equation (2).

The values of interaction energy of different types of cation and cation hole, anion and anion hole are as follows;

$E_{\dot{A}}$: 5.2 K cal/mol for KCl-LiCl system,

$E_{\dot{A}}$: 3.6 K cal/mol for KCl-NaCl system,

$E_{\dot{A}}$: 3.0 K cal/mol for KCl-KBr and NaCl-NaBr systems.

The value of interaction energy corresponds to the ratio of the ionic radius of K^+ ion to the ionic radius Li^+ ion or Na^+ ion.

It may be concluded therefore that the deviation of the values of activation

Table 6. Activation energy for ionic conductance in KCl-LiCl and KCl-NaCl systems.

Composition (mol%)		Calc. with eq. (8) (K cal/mol)		Calc. with eq. (2) (K cal/mol)
KCl	LiCl	total energy	excess energy of mixing*	
100	0	3.32	0	3.32
80	20	3.85	0.88	3.84
60	40	3.94	1.33	3.70
40	60	3.60	1.33	3.68
20	80	2.78	0.88	2.78
0	100	1.56	0	1.56
KCl	NaCl			
80	20	3.39	0.19	3.40
60	40	3.35	0.29	3.43
40	60	3.23	0.29	3.24
20	80	3.00	0.19	3.00
0	100	2.67	0	2.67

*: $2x_1 x_2 \{E_{\dot{A}} - 2(E_A + E_B)\}$

Table 7.   Activation energy for ionic conductance in KCl-KBr and NaCl-NaBr systems.

Composition (mol%)		Calc. with eq. (8) (K cal/mol)		Calc. with eq. (2) (K cal/mol)
KCl	KBr	total energy	excess energy of mixing	
80	20	3.29	−0.20	3.29
60	40	3.28	−0.32	3.y6
40	60	3.35	−0.32	3.31
20	80	3.56	−0.20	3.50
0	100	3.86	0	3.86
NaCl	NaBr			
80	20	2.90	0.04	2.89
60	40	2.89	0.06	2.86
40	60	2.91	0.06	2.84
20	80	2.90	0.04	2.90
0	100	2.86	0	2.86

energy for ionic conductance from additivity of the molar compositions is caused by the interactions between different types of cation and cation hole or anion and anion hole in the liquid mixture in these systems.

6. Summary

We measured the electrical conductivity of KCl-LiCl, KCl-NaCl, KCl-KBr and NaCl-NaBr systems.

In the KCl-LiCl and KCl-NaCl systems, the isotherms of equivalent conductivity of these systems showed negative deviation from additivity of molar compositions, and the activation energy for ionic conductance showed positive deviation from additivity.

In the KCl-KBr and NaCl-NaBr systems, the isotherms of equivalent conductivity of these systems showed positive deviation from additivity but the degree of negative deviation from additivity was smaller than KCl-LiCl and KCl-NaCl systems, the activation energy of the KCl-KBr system showed negative deviation from additivity, but in the NaCl-NaBr system, the activation energy was almost linear in all compositions.

The deviations of activation energy for ionic conductance from additivity are caused by the interaction between different types of cation and cation hole or anion and anion hole in these mixtures, and the activation energy for ionic conductance of fused KCl-LiCl, KCl-NaCl, KCl-KBr and NaCl-NaBr mixtures may be represented by equation (8).

References

1) B. Poincare, Ann. Chim. Phys., 21, 289 (1890)
2) I.S. Yaffe & Van Artsdalen, J. Phys. Chem., 59, 118 (1955)
3) H. Bloom & E. Heymann, Proc. Roy. Soc., 188, 392 (1947)
4) J.O'M. Bockris, "Modern Aspects of Electrochemisty" No. 2. Butterworth Scientific Pub. 160 (1959)
5) J. Frenkel, Kinetic Theory of Liquid Dover, 40 (1955)
6) R.A. Swalin, Thermodynamics of Solids John Wiley & Sons, 109 (1961)
7) E. Elchardus & P. Laffitte, Bull, Soc. chim. France, 51, 1572 (1932)
8) J.O'M. Bockris, Proc. Roy. Soc., 241, 554 (1957)