Local Structure and Okada's Empirical Relation for the Internal Mobility of Cations in Molten Alkali Nitrates

Junko Habasaki

Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

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The empirical relation

$$b_i = (V - V_{0i})^{-1} A_i \exp(-E_i/RT)$$

for the internal mobility b_i of cations i in mixtures of molten alkali nitrates, where V is the molar volume of the mixture, is compared with MD simulations. For pure $LiNO_3$ and $NaNO_3$ it is found that $(V-V_{0i})^{-1}$ is proportional to the concentration of oxygens in the first coordination shells of the cations i.

From countercurrent electromigration [1] measurements of internal mobilities b_i of cations i in molten binary and ternary alkali nitrate mixtures, the empirical relation

$$b_i = (V - V_{0i})^{-1} A_i \exp(-E_i/RT) \quad (1)$$

has been derived by Okada and coworkers [2–11]. This relation involves the molar volume V of the mixture and a parameter V_{0i} which depends on the type of cation i. In such mixtures the number of oxygen atoms per macroscopic unit volume is

$$n = 3N_A/V, \quad (2)$$

where N_A is Avogadro's number.

According to (1), positive (negative) values of V_{0i} tell us that the concentration of oxygens is greater (smaller) than n in the microscopic regions which are decisive for the magnitude of b_i. If these regions are considered to be the first oxygen coordination shells around the cation i, the relation

$$3N_A/(V - V_{0i}) \approx N_{1i}/v_{1i} \quad (3)$$

should hold, where N_{1i} is the oxygen atom content of these shells and v_{1i} their volume.

It is the aim of this note to check the validity of (3) by inserting empirical values of $V - V_{0i}$ and N_{1i}/v_{1i}, the latter being derived from molecular dynamics (MD) simulations and X-ray and neutron diffraction studies [12].

The references for the alkali nitrate systems so far studied are given in Table 1 and the empirical parameters of (1) for some alkali nitrates are given in Table 2. The parameters for the cases i = Rb and i = Cs, where negative values of V_{0i} were found [13], will be discussed elsewhere.

The values $V - V_{0i}$ were calculated for several molar volumes of the mixtures, as shown in Table 3.

Table 1. The systems so far studied.

M_i \ M_j	Na	K	Rb	Cs	Na, K
Li	[2]	[4] [5]	[7]	[7]	[11]
Na		[2]	[8]	[2]	
K			[6]	[3] [10]	
Rb				[9]	

Table 2. Parameters A_i, E_i, V_{0i}.

	$A_i \times 10^{11}$ $m^5 V^{-1} s^{-1} mol^{-1}$	E_i $kJ\,mol^{-1}$	V_{0i} $cm^3\,mol^{-1}$
M_i			
Li [2]	2.84	17.80	24.7
Na [2]	4.94	19.71	24.2*
K [3]	4.21	16.74	10.5
[10]	3.95	18.00	22.1

* The small temperature dependence of V_{0i} observed for the system is neglected here.

Table 3. Values of $V - V_{0i}$ for several V values of the mixtures. V and V_{0i} in $cm^3\,mol^{-1}$.

V	45	50	60
M_i			
Li	20.3	25.3	35.3
Na	20.8	25.8	35.8
K*	34.5	39.5	49.5

* The V_{0i} value of [3] was used.

Reprint requests to Dr. Junko Habasaki, Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta 4259, Midori-ku, Yokohama 227, Japan.

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The volume of the first oxygen coordination shell was taken to be

$$v_1 = (4/3)\pi(r_2^3 - r_1^3), \tag{4}$$

where r_1 and r_2 are the distances from the cation where the corresponding $g(r)$ crosses unity for the first and second time, respectively [14].

An MD simulation of molten $LiNO_3$ at 550 K [12] gave $r_{1Li} = 1.65$ Å, $r_{2Li} = 2.29$ Å and $N_{1Li} = 4.2$. These data coincide well with the data obtained by X-ray diffraction and neutron diffraction. When using these values, N_{1Li}/v_{1Li} turns out to be 1.33×10^{23} cm^{-3}. On the other hand, the left hand side of (3) becomes 1.26×10^{23} cm^{-3} when using the V_{0Li} value in Table 2.

An MD simulation of molten $NaNO_3$ has been carried out at 650 K [15]. The values of r_{1Na}, r_{2Na} and N_{1Na} were found to be 2.05 Å, 2.93 Å and 5.40, respectively. With these the value 7.79×10^{22} cm^{-3} was obtained for the right hand side of (3), while 8.36×10^{22} cm^{-3} was obtained for the left hand side of (3).

This coincidence seems to prove that b_i is indeed proportional to the concentration of oxygens in the first oxygen coordination shell around the cation i. A definite answer, however, can only be given when (3) has also been checked for mixtures of alkali nitrate melts. This shall be done in a future study.

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