

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

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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

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

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

$$n = 3 N_A/V, \tag{2}$$

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

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

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} ,

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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 $i = \text{Rb}$ and $i = \text{Cs}$, 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.

$M_i \backslash M_j$	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} .

M_i	$A_i \times 10^{11}$ $\text{m}^5 \text{V}^{-1} \text{s}^{-1} \text{mol}^{-1}$	E_i kJ mol^{-1}	V_{0i} $\text{cm}^3 \text{mol}^{-1}$
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 $\text{cm}^3 \text{mol}^{-1}$.

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.

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

$$v_1 = (4/3)\pi(r_2^3 - r_1^3), \quad (4)$$

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 $r_{1\text{Li}} = 1.65 \text{ \AA}$, $r_{2\text{Li}} = 2.29 \text{ \AA}$ and $N_{1\text{Li}} = 4.2$. These data coincide well with the data obtained by X-ray diffraction and neutron diffraction. When using these values, $N_{1\text{Li}}/v_{1\text{Li}}$ turns out to be $1.33 \times 10^{23} \text{ cm}^{-3}$. On the other hand, the left hand side of (3) becomes $1.26 \times 10^{23} \text{ cm}^{-3}$ when using the $V_{0\text{Li}}$ value in Table 2.

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

- [1] A. Klemm, H. Hintenberger and P. Hoernes, Z. Naturforsch. **2a**, 245 (1947).
- [2] C. Yang, R. Takagi, and I. Okada, ibd. **35a**, 1186 (1980).
- [3] C. Yang, R. Takagi, and I. Okada, ibd. **38a**, 135 (1983).
- [4] A. Lundén and I. Okada, ibd. **38a**, 97 (1983).
- [5] A. Lundén, J. Habasaki, and I. Okada, ibd. **42a**, 683 (1987).
- [6] A. Ekhed and A. Lundén, ibd. **34a**, 1207 (1979).
- [7] I. Okada, R. Takagi, and K. Kawamura, ibd. **34a**, 381 (1981).
- [8] I. Okada, R. Takagi, and K. Kawamura, ibd. **36a**, 381 (1981).
- [9] R. Takagi, K. Kawamura, and I. Okada, ibd. **39a**, 759 (1984).
- [10] M. Chemla and I. Okada (1988) unpublished result.
- [11] J. Habasaki and I. Okada, Z. Naturforsch. **40a**, 906 (1985).
- [12] T. Yamaguchi, I. Okada, H. Ohtaki, M. Mikami, and K. Kawamura, Mol. Phys. **58**, 349 (1986).
- [13] C. Yang, thesis of doctor courses, Tokyo Institute of Technology, Yokohama 1988.
- [14] G. Palinkas, W. O. Riede, and K. Heinzinger, Z. Naturforsch. **32a**, 1137 (1977).
- [15] A. K. Adya, R. Takagi, K. Kawamura, and M. Mikami, Mol. Phys. **62**, 227 (1987). — I. Okada et al., unpublished result.