Internal Cation Mobilities in the Molten Systems (Li-Na)NO_3 and (Na-Cs)NO_3

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Z. Naturforsch. **35a**, 1186–1191 (1980); received August 19, 1980

For the molten salt systems (Li-Na)NO_3 and (Na-Cs)NO_3, relative differences of internal mobilities have been measured with the Klemm method. The internal mobilities, b, are calculated from these data and the available conductivity data. In the mixtures of the former system, b_{Na} is always greater than b_{Li}. In the latter system, the Chemla crossing point occurs. It is found that b_{Li} and b_{Na} in the binary alkali nitrate systems so far investigated are well expressed, except at small molar volumes, by $b = \{A/(V - V^0)\} \exp(-E/RT)$ with constant A and E, where V is the molar volume and V^0 a constant for b_{Li} and nearly a constant for b_{Na}. The values of b_{Cs} at equal concentrations of $CsNO_3$ in the systems (Li-Cs)NO_3 and (Na-Cs)NO_3 are practically equal. The internal mobilities obtained are discussed in terms of free space, mutual ionic attraction and thermal agitation.

Introduction

In a previous work internal mobilities of the systems (Li-Rb)NO_3 and (Li-Cs)NO_3 had been measured [1]. It was found that these systems show the effect discovered by Chemla and coworkers [2–4], i.e. that the difference of the internal mobilities of two pure salts with a common ion changes sign on mixing in certain ranges of temperature and composition. Analogous effects have recently been shown to occur in molecular dynamics simulations of the systems (Li-K)Br [5] and (Li-Rb)Cl [6]. Measurements of external mobilities with the paper strip method on the systems (Na-K)NO_3 [4, 7] and (Na-Cs)NO_3 [8] did also show the Chemla effect.

In order to augment our knowledge of these phenomena, in the present study the Klemm method, i.e., a countercurrent electromigration method is employed for the measurement of the relative differences in internal cationic mobilities of the systems (Li-Na)NO_3 and (Li-Cs)NO_3. In the following, these systems will be referred to as (I) and (II), respectively. We believe that this method is one of the most reliable and convenient methods for the present purpose. Internal mobilities are calculated from the available data on the molar conductivities of these systems, and a discussion of the results closes the paper.

Experimental

The chemicals $LiNO_3$, $NaNO_3$ and $CsNO_3$ (reagent grade) were melted, bubbled with dry nitrogen gas for about 1 h, solidified and stored in a desiccator. Prescribed amounts of the salts were melted together in a quartz vessel. After sufficient mixing, a separation tube (internal diameter: 4 mm) packed with quartz powder of 80–100 mesh was put into the vessel. The filled quartz-diaphragm, about 20 cm long, was then inserted in an electromigration cell, and electromigration was started immediately. The arrangement of the cell has been previously described [1]. With a temperature controller the temperature could be kept within ±1 °C in most runs. The low temperature isotherm taken still allowed for a sufficient range of compositions according to the phase diagram ([9] for (I) and [10] for (II)). After electromigration (about 7 hours), the tube was taken out, and the part near the anode was cut into about 10 pieces, ca. 1.0 cm long. The content of cations in each piece was determined by flame spectrophotometry (Li and Na) and atomic absorption spectrophotometry (Cs). In the analysis of Cs, KNO_3 was added (≈ 1000 ppm) to suppress the ionization of Cs.

Results

The relative differences, ε, in internal mobilities, b, of two cations, defined by

$$\varepsilon_{12} = (b_1 - b_2)/\bar{b} \qquad (1)$$

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and calculated from the amounts of the cations in the separation tube and the transported charge [11], are given along with relevant experimental data in Tables 1 and 2. In (1), the suffixes 1 and 2 refer to the cation with the larger and smaller b in the corresponding pure salt, respectively, and b is given by

$$\bar{b} = p_1 b_1 + p_2 b_2 = \Lambda/F\,, \tag{2}$$

where the p's are the mole fractions of the mixture, Λ is the molar conductivity and F the Faraday constant.

From (1) and (2), one obtains

$$b_1 = (\Lambda/F)\,(1 + p_2\,\varepsilon_{12})\,, \tag{3}$$

$$b_2 = (\Lambda/F)\,(1 - p_1\,\varepsilon_{12})\,. \tag{4}$$

The values of Λ were obtained from the available data on electrolytic conductivities of (I) [12] and (II) [13] and on densities [14]. The isotherms of b_1 and b_2 are shown for (I) at 573 and 653 K in Fig. 1 and for (II) at 600 and 723 K in Figure 2.

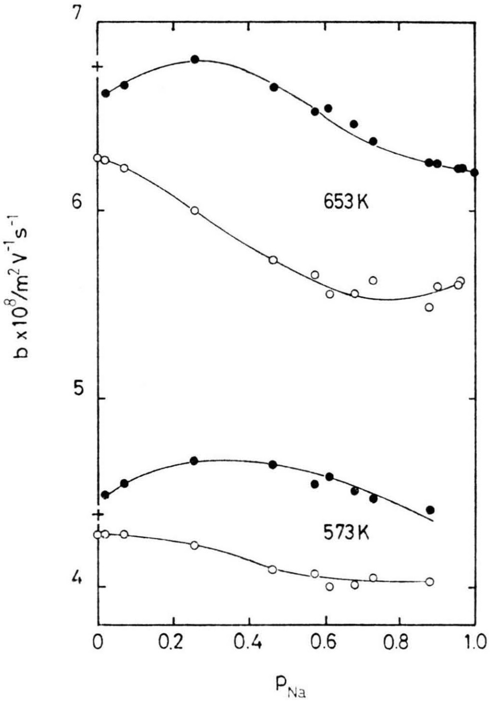

Fig. 1. Isotherms of internal cation mobilities in the system (Li-Na)NO_3. ○: b_{Li}; ●: b_{Na}; +: b_{Na}, evaluated from external mobility, in the system (Li-K)NO_3 ($p_K = 0.01$) [16].

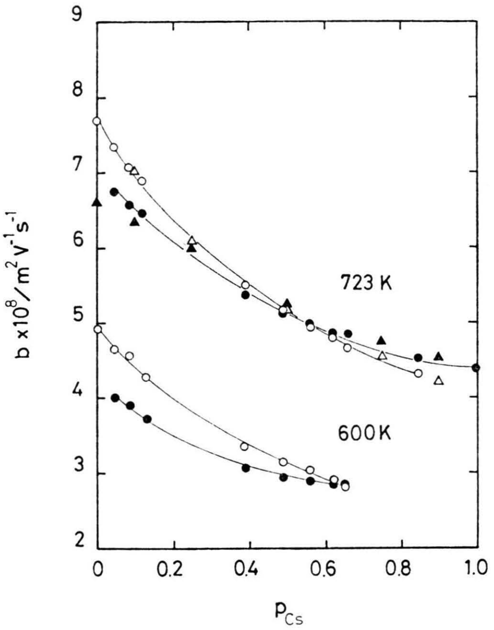

Fig. 2. Isotherms of internal cation mobilities in the system (Na-Cs)NO_3. ○: b_{Na}; △: b_{Na}, evaluated from external mobility, [8]; ●: b_{Cs}; ▲: b_{Cs}, evaluated from external mobility, [8].

Discussion

The negative sign of ε_{12} in Table 1 shows that the mobility of Na^+ is always greater than that of Li^+. (Li-Na)NO_3 is thus a system where the Chemla effect occurs at all temperatures and compositions.

In a molten (Li-Na)NO_3 mixture, Lantelme and Chemla enriched ^7Li by countercurrent electromigration [15]. In their experiment, the molar ratio $LiNO_3/NaNO_3$ at the anode was initially 0.7 ($p_{Na} = 0.59$) and seemed to become stationary at a value of 1.4 ($p_{Na} = 0.42$) after electromigration of 30 days at 340 °C. If this signifies that the Chemla crossing point occurs at this composition at 340 °C, this is in contrast to our results.

In other experiments, Lantelme and Chemla measured the external mobilities in the (Li-K)NO_3 system containing a trace amount of Na^+ with a paper strip method [16]. Their data at a concentration of 99 mol% $LiNO_3$ may be compared with ours for (I). The internal mobilities of Na^+ estimated from their data are shown in Fig. 1 for comparison. They are in satisfactory agreement with ours.

In a previous molecular dynamics study we have shown that the internal mobility is closely related with the self-exchange velocity of neighbouring

Table 1. Conditions and the results for the system (Li-Na)NO_3. Q is the transported charge.

Run	T/K	p_{Na}	Q/C	ε_{12}
1	618	0.959 ± 0.001	2521	−0.089 ± 0.004
2	663		2361	−0.094 ± 0.007
3	692		2299	−0.108 ± 0.005
4	608	0.955 ± 0.001	2541	−0.091 ± 0.003
5	645		2302	−0.099 ± 0.005
6	676		2462	−0.105 ± 0.005
7	687		2356	−0.105 ± 0.004
8	597	0.901 ± 0.001	2274	−0.095 ± 0.004
9	660		2265	−0.110 ± 0.007
10	683		2361	−0.111 ± 0.004
11	575	0.881 ± 0.003	2430	−0.084 ± 0.004
12	590		2909	−0.092 ± 0.009
13	628		2073	−0.106 ± 0.014
14	696		2489	−0.118 ± 0.008
15	553	0.731 ± 0.005	2430	−0.082 ± 0.005
16	610		2231	−0.115 ± 0.007
17	627		2000	−0.118 ± 0.010
18	648		2239	−0.115 ± 0.009
19	557	0.679 ± 0.002	2272	−0.111 ± 0.002
20	571		2372	−0.112 ± 0.002
21	609		2396	−0.130 ± 0.003
22	662		2237	−0.149 ± 0.003
23	536	0.609 ± 0.002	2599	−0.138 ± 0.003
24	583		2625	−0.149 ± 0.002
25	629		2115	−0.155 ± 0.002
26	663		1933	−0.166 ± 0.007
27	549	0.572 ± 0.004	2266	−0.100 ± 0.004
28	641		1909	−0.140 ± 0.005
29	662		1884	−0.150 ± 0.003
30	563	0.459 ± 0.003	2909	−0.125 ± 0.009
31	647		2842	−0.149 ± 0.008
32	551	0.255 ± 0.004	2253	−0.097 ± 0.004
33	583		2139	−0.109 ± 0.003
34	616		2243	−0.122 ± 0.003
35	655		2053	−0.130 ± 0.005
36	565	0.069 ± 0.001	2100	−0.060 ± 0.002
37	603		2330	−0.068 ± 0.002
38	615		2388	−0.071 ± 0.001
39	656		2276	−0.065 ± 0.001
40	550	0.018 ± 0.002	2759	−0.050 ± 0.001
41	584		2515	−0.046 ± 0.001
42	613		2644	−0.053 ± 0.003
43	666		2801	−0.061 ± 0.002
44	681		2806	−0.058 ± 0.001

unlike ions [6]. Thus, in the following we will interpret mobilities mainly in the way self-exchange velocities are to be interpreted.

A decrease of b_{Li} with increasing concentration of the larger cation is commonly observed in other systems. In (I) this decrease is rather moderate (see Figure 1). This is probably because the free space does not increase much with increasing concentration of $NaNO_3$. Particularly at higher concentrations of $NaNO_3$, the isotherms of b_{Li} are nearly horizontal. This apparent concentration independence of b_{Li} might be caused by a change of the most probable configurational position of the Li^+ ions around the NO_3^- ions in the $NaNO_3$ rich region. From an X-ray diffraction study on molten alkali nitrates, Ohno and Furukawa suggest that pure molten $LiNO_3$ and $NaNO_3$ exhibit different angular distributions of the cations around the anions [17].

b_{Na} decreases at high concentrations of $LiNO_3$, and the peak of the isotherm moves toward higher concentrations of $LiNO_3$ with increasing temperature (see Figure 1). This trend for the large cation is known from other systems such as (Li-Rb)NO_3 [1], (Li-Cs)NO_3 [1] and (Li-Tl)NO_3 [18].

As for (II), our values have to be extrapolated to a somewhat higher temperature to be compared with data obtained with the paper strip method at 723 K by Kwak and Ketelaar [8]. Figure 2 shows that our results are in good agreement with theirs. The Chemla crossing point moves toward higher concentrations of the smaller cation with temperature, as is commonly found [19]. Our interpretation for this has been described in [6].

In order to compare the internal mobilities in (II) with those in the system (Li-Cs)NO_3 [1] (this system will be referred to as (III) in the following), the isotherms of b in both the systems at 623 and 673 K are shown in Figure 3. The values of b_{Cs} at $p_{Cs} = 0$ are evaluated from the external mobilities of trace amounts of ^{137}Cs in pure $LiNO_3$ and $NaNO_3$ [20] and from the external transport numbers of pure $LiNO_3$ and $NaNO_3$ [21], respectively. They agree well with those extrapolated from our results. The isotherms of b_{Li} decrease more sharply than those of b_{Na} with increasing $CsNO_3$ concentration. This can be interpreted as follows: The increase of free space with increasing $CsNO_3$ concentration is larger in (III) than in (II). Further, the pair potential well is deeper for Li^+-NO_3^- than for Na^+-NO_3^-. When the distance between two neighbouring NO_3^- ions is relatively large, a Li^+ ion is more strongly attracted to its reference NO_3^- ion than a Na^+ ion is. Therefore, Li^+ leaves its reference NO_3^- ion less easily than Na^+ does, as the concentration of $CsNO_3$ increases.

Figure 3 also reveals that b_{Cs} in both systems is independent of the sort of coexisting cations except at very low mole fractions, although the free space

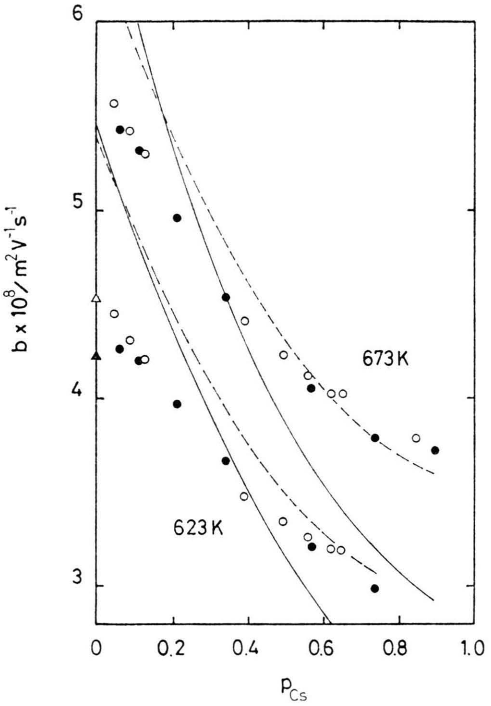

Fig. 3. Isotherms of internal cation mobilities in the systems (Li-Cs)NO_3 [1] and (Na-Cs)NO_3. ——: b_{Li}; ---: b_{Na}; ●: b_{Cs} in (Li-Cs)NO_3; ○: b_{Cs} in (Na-Cs)NO_3; ▲: $b_{Cs}{}^a$ in $LiNO_3$ [20]; △: $b_{Cs}{}^a$ in $NaNO_3$ [20].
[a] evaluated from external mobility.

decreases more quickly in (III) than in (II) with decreasing concentration of $CsNO_3$. As an "agitator", however, Li^+ is more effective than Na^+. Since b_{Cs} increases with decreasing mole fraction of $CsNO_3$, the agitation effect evidently dominates over the free space effect, and since b_{Cs} is substantially the same in (II) and (III), the difference of the agitation effect between (II) and (III) seems incidentally to be compensated by the free-space effect. At very low concentrations of $CsNO_3$, b_{Cs} in (III) tends to decrease with decreasing concentration of $CsNO_3$, whereas b_{Cs} in (II) does not.

As for the external mobility of Cs^+ at $p_{Cs} = 0$, it is greater in $LiNO_3$ than in $NaNO_3$ (3.33 and 2.95 $\times 10^{-8}\,m^2\,V^{-1}\,s^{-1}$ in $LiNO_3$ and $NaNO_3$, respectively, at 623 K [20]). These facts suggest that the free space at very high concentration of $LiNO_3$ is critically small for the movement of NO_3^- but not for Cs^+, while at very high concentration of $NaNO_3$ it is not too small even for NO_3^-.

We have previously stated that there exists a relation between b_{Li} and the molar volume, V, of molten binary alkali nitrate systems, irrespective of the sort and concentration of coexisting cations [1]. We now furthermore find that b_{Li} and b_{Na} in such systems can well be represented, except for small molar volumes, by the equation

$$b = \frac{A}{(V - V^0)} \exp\left\{-\frac{E}{RT}\right\}, \qquad (5)$$

where A and E are constants and V^0 is constant for b_{Li} and slightly temperature dependent for b_{Na}. In Fig. 4, the isotherms of $(1/b_{Li})$ at 3 temperatures are plotted against the molar volume. The solid lines are drawn with the following parameters: $A = 2.84 \times 10^{-11}\,m^5\,V^{-1}\,s^{-1}\,mol^{-1}$, $E = 17.8\,kJ\,mol^{-1}$ and $V^0 = 24.7\,cm^3\,mol^{-1}$. In Fig. 5 the values of $(1/b_{Na})$

Table 2. Conditions and the results for the system (Na-Cs)NO_3. Q is the transported charge.

Run	T/K	p_{Cs}	Q/C	ε_{12}
101	671	0.844 ± 0.001	2161	−0.042 ± 0.006
102	695		2086	−0.043 ± 0.003
103	704		1999	−0.043 ± 0.007
104	588	0.651 ± 0.001	1379	0.006 ± 0.002
105	605		1873	−0.012 ± 0.010
106	671		1840	−0.025 ± 0.005
107	615	0.620 ± 0.002	2053	0.027 ± 0.004
108	637		2136	0.023 ± 0.006
109	652		2374	0.005 ± 0.004
110	689		1739	0.006 ± 0.005
111	581	0.561 ± 0.001	1870	0.060 ± 0.005
112	609		2143	0.048 ± 0.004
113	649		2438	0.025 ± 0.003
114	706		1930	0.001 ± 0.002
115	574	0.494 ± 0.002	1805	0.092 ± 0.004
116	609		1782	0.057 ± 0.004
117	628		2197	0.044 ± 0.002
118	667		1440	0.036 ± 0.004
119	681		1850	0.030 ± 0.003
120	569	0.389 ± 0.002	2183	0.115 ± 0.004
121	593		2417	0.101 ± 0.006
122	641		2112	0.072 ± 0.004
123	679		2227	0.052 ± 0.004
124	691		1678	0.044 ± 0.005
125	591	0.126 ± 0.001	2059	0.146 ± 0.003
126	616		2599	0.114 ± 0.004
127	668		2264	0.083 ± 0.003
128	679		2334	0.086 ± 0.005
129	610	0.084 ± 0.002	1906	0.144 ± 0.002
130	648		2065	0.106 ± 0.004
131	667		2244	0.103 ± 0.007
132	670		2142	0.105 ± 0.004
133	604	0.046 ± 0.001	1903	0.143 ± 0.006
134	637		2367	0.134 ± 0.006
135	671		2820	0.113 ± 0.005

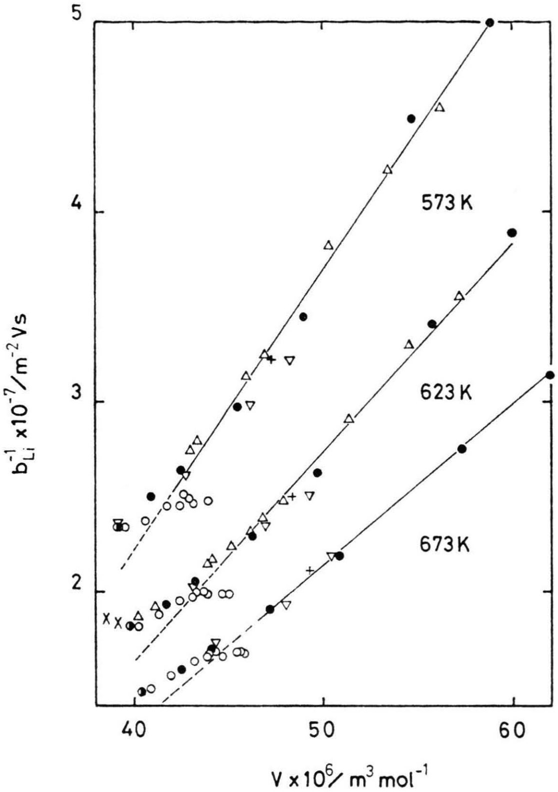

Fig. 4. The reciprocal of internal mobilities of Li^+ vs. molar volume in binary systems (Li-M)NO_3. ◑: M = Li[a]; ○: Na; +: K [24]; ▽ [b]: K [16]; △: Rb [1]; ●: Cs [1]; ×: Li[a] at high pressure at 623 K [22, 23].

[a] pure $LiNO_3$, [b] evaluated from external mobility.

are similarly plotted, the parameters for the solid lines being $A = 4.30 \times 10^{-11}$ m^5 V^{-1} s^{-1} mol^{-1}, $E =$ 18.9 kJ mol^{-1} and $V^0 = 25.3$, 24.2 and 23.2 cm^3 mol^{-1} at 600, 623 and 673 K, respectively. These parameters, however, are substantially calculated from (II) only. Thus, more data on other systems are needed to learn whether V^0 really depends on temperature for b_{Na}. Measurements of the systems (Na-K)NO_3 and (Na-Rb)NO_3 are in progress.

Figures 4 and 5 indicate that b_{Li} and b_{Na} depend on the sort and concentration of the coexisting cations only via the molar volume, as far as V is not too small. Since the polarization effect is expected to depend on the sort and concentration of coexisting cations, this implies that it plays a minor role, if any, in the mobility of Li^+ and Na^+, at least in the large molar volume region. This also means that associated species, whose concentration should depend on concentration, are not likely to occur in electric transport in this case.

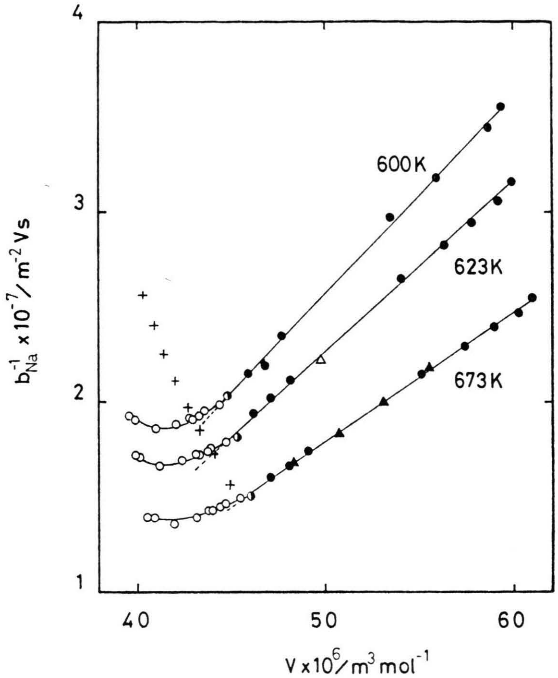

Fig. 5. The reciprocal of internal mobilities of Na^+ vs. molar volume in binary systems (Na-M)NO_3. ○: M = Li; ◑: Na[a]; ▲[b]: K [4]; △[b]: K [7]; ●: Cs; +: Na[a] at high pressure at 673 K [22, 23].

[a] pure $NaNO_3$, [b] evaluated from external mobility.

The systematic upward deviations from the straight lines in Figs. 4 and 5 below certain V-values V^d suggest that the free space becomes critically small. The values of V^d for b_{Li} seem to be independent of coexisting cations. The values of $(1/b_{Na})$ clearly deviate from the solid lines below V^d and even start to increase at some V-value smaller than V^d. The values of V^d are slightly smaller for b_{Li} than for b_{Na} at the same temperatures, as seen from Figs. 4 and 5. This is quite reasonable, since a Li^+ ion is smaller than a Na^+ ion.

The values of $(1/b_{Li})$ at 623 K and $(1/b_{Na})$ at 673 K calculated from the data for pure $LiNO_3$ and $NaNO_3$ under high pressure [22, 23] are also plotted in Figs. 4 and 5, respectively. The values of b_{Na} under high pressure are much smaller than those for (I) under ambient pressure. This is partly because the free space is smaller in pure $NaNO_3$ under high pressure than in (I) under ambient pressure at given values of V, and partly because the agitation effect of Li^+ is more effective than that of Na^+. It is not clear whether these two reasons alone can explain the large difference between b_{Na} under high pressure and that in (I) under ambient pressure.

In conclusion, the general features of the internal mobilities of the cations in (I) and (II) can be understood in the sense of our molecular dynamics study of the molten (Li-Rb)Cl [6]. It is confirmed that the free space plays a significant role. It is often argued that Li^+ ions behave anomalously in transport phenomena such as electric conductivity. This is, however, probably caused by the small amount of free space which salts containing Li^+ ions produce, and Li^+ ions themselves must behave rather normally.

Acknowledgement

We are sincerely grateful to Professor A. Klemm for his valuable comments and suggestions.

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