The Electrical Conductivity of Molten Lithium Sulphate with Small Quantities of Foreign Cations

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The electrical conductivity of molten lithium sulphate with small quantities of foreign cations (Na^+, K^+, Rb^+, Cs^+, Mn^{++}, Cd^{++} and Ba^{++}) has been measured from 700 to 950 °C. The temperature dependence of the specific conductivity can in all cases with good accuracy be described by straight lines. The decrease in the specific conductivity is approximately proportional to the volume of the foreign cation. If it is assumed that the cations are moving in groups, the number of ions in each group is found to be 2.7. The change in free volume of molten lithium sulphate, when a small quantity of foreign ions is added, seems to have little importance for the change in electrical conductivity. An estimation of the mobility of Cd^{++} ions indicates the existens of WAGNER effect in molten lithium sulphate.

Little is known about the changes in transport properties of a pure molten salt, when small quantities of foreign ions are added, though intense studies of such systems have been made in the solid state.

Several conditions must be fullfilled to make measurements of the electrical conductivity of pure salts with small quantities of impurities; the change in conductivity must be comparably big when the foreign ions are added and the reproducibility of the results must be good.

CLEAVER, RHODES and UBBELOHDE [1] have found that the conductivity of molten KNO_3 decreases on adding $Ba(NO_3)_2$, in contrast to solid KNO_3. As a probable explanation to this was proposed that there is an electrostrictive shrinkage of the free volume when the divalent cations are added to the melt. PAPIANNOU and HARRINGTON [2] have measured the electrical conductivity of nitrates with small quantities of Co^{2+} and Ni^{2+} ions, but their results are complicated [3].

It has been found by the author [4] that the decrease in electrical conductivity of pure molten lithium sulphate is almost 8%, when 3 mole % of potassium sulphate is added and it was therefore assumed that this change should be big also when other univalent or divalent sulphates were added. We have thus made a systematical investigation, using Na^+, K^+, Rb^+, Cs^+, Mg^{++}, Cd^{++} and Ba^{++} ions as impurities. Fe^{++} ions were also tried, but it was found that the decomposition of this salt was considerable.

All salts were analytical grade and were used without further purification. The chemicals were dried at least for 1 day at 180 °C, $MgSO_4$ at 220 °C.

The experimental technique is described elsewhere in detail [5]. The salts were mixed and melted in vacuum in quartz capillary cells, but several of the measurements were performed in argon atmosphere. Only very slight corrosion of the cells was observed, except when $Li_2SO_4-Na_2SO_4$ and $Li_2SO_4-MgSO_4$ mixtures were used. This attack could however be somewhat reduced by keeping the salts completely free from water.

Results

The results are summarized in Table 1. The spezific electrical conductivities can with good accuracy be described by straight lines

$$\varkappa = a\,t + b$$

where $\varkappa$ is the specific conductivity, a und b constants, and t the temperature in °C. The standard deviation [6]

$$s = \sqrt{\Sigma(\varkappa-\varkappa_{\mathrm{m}})^2/(n-1)}$$

is in all cases less than 0.3%. $\varkappa-\varkappa_{\mathrm{m}}$ is the difference between the measured value and the value obtained from the regression line and n is the number of measured values.

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Impurity	Mole-% impurities	Temperature interval °C		$a \cdot 10^3$ $\Omega^{-1}\,cm^{-1}\,°C^{-1}$	b $\Omega^{-1}\,cm^{-1}$	s $\Omega^{-1}\,cm^{-1}$	$\varkappa_{890}$ $\Omega^{-1}\,cm^{-1}$	$-\Delta\varkappa$ $\Omega^{-1}\,cm^{-1}$	$-\Delta\varkappa/n$ $\Omega^{-1}\,cm^{-1}$	$(-\Delta\varkappa/n)_{MV}$ $\Omega^{-1}\,cm^{-1}$
—	—	866	930	5.4488	0.516	0.008	4.333	—	—	—
Na_2SO_4	2.00	866	917	5.4453	0.577	0.008	4.269	0.064	0.032	0.045
Na_2SO_4	4.89	843	909	5.0930	0.505	0.001	4.048	0.285	0.058	
K_2SO_4	3.00	825	904	5.3295	0.737	0.004	4.006	0.327	0.109	0.106
K_2SO_4	4.89	770	911	5.3530	0.935	0.007	3.829	0.504	0.103	
Rb_2SO_4	2.00	820	887	5.3085	0.677	0.006	4.048	0.285	0.143	0.150
Rb_2SO_4	6.51	699	853	5.2663	1.369	0.006	3.318	1.015	0.156	
Cs_2SO_4	2.00	818	895	5.5353	1.026	0.007	3.900	0.433	0.217	0.199
Cs_2SO_4	4.89	764	859	5.0831	1.083	0.003	3.441	0.892	0.181	
$MgSO_4$	4.00	838	950	5.7575	0.934	0.011	4.190	0.143	0.036	0.036
$CdSO_4$	3.92	841	895	5.3065	0.478	0.009	4.245	0.088	0.022	0.022
$BaSO_4$	3.92	826	918	5.1399	0.519	0.003	4.056	0.277	0.071	0.071

Table 1. The specific electrical conductivity $\varkappa = aT + b$ of molten lithium sulphate with small quantities of other sulphates. s is the standard deviation and $\Delta\varkappa$ the difference between the conductivity of pure Li_2SO_4 and the mixtures at 890 °C. n is the number of mole per cent impurities and $(\Delta\varkappa/n)_{MV}$ the mean value of the change of $\varkappa$ per mole per cent impurities.

Both with univalent and divalent impurity ions, the change in the temperature dependence of the specific conductivity is small (less than 7%), but the constant b changes considerably.

We have also calculated the change in specific conductivity

$$\Delta\varkappa = \varkappa(\text{mixture}) - \varkappa(Li_2SO_4)$$

when the foreign ions are added; $\Delta\varkappa$ is always negative. In Fig. 1 we have plotted $\Delta\varkappa$ as a function of the quantity of univalent impurity ions. It is possible to draw four straight lines through these points. The slope of the lines is increasing with increasing size of the foreign ions, and we therefore also plotted the change in conductivity per mole per cent impurities ($\Delta\varkappa/n$) as a function of the volume of the foreign cations (Fig. 2), where we have used PAULING radii. It is seen that a straight line is obtained and $\Delta\varkappa/n$ with Cd^{++} and Ba^{++} ions is also on the same straight line as the univalent ions. There is however no reason to believe that the connection between the ionic volume and the specific electrical conductivity has a physical meaning (see below).

The results obtained with 4.00 mole per cent $MgSO_4$ are less reliable, since the corrosion of the cell was considerable.

Discussion

In the foregoing we have only considered the specific electrical conductivity. As for the density when two salts are mixed, JAMES and LIU [7] have found that

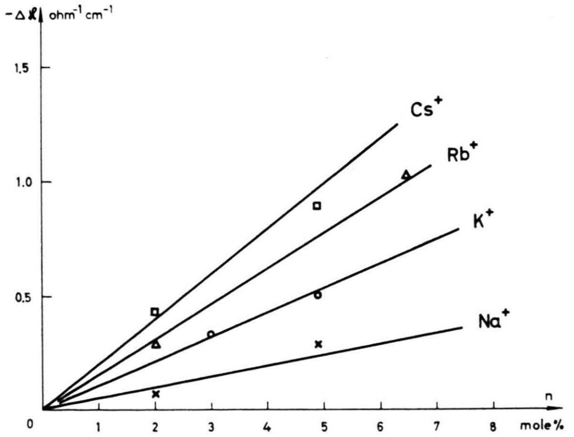

Fig. 1. The change in electrical conductivity of molten lithium sulphate, when small quantities of foreign cations are added as a function of the quantity of M_2SO_4 at 890 °C.

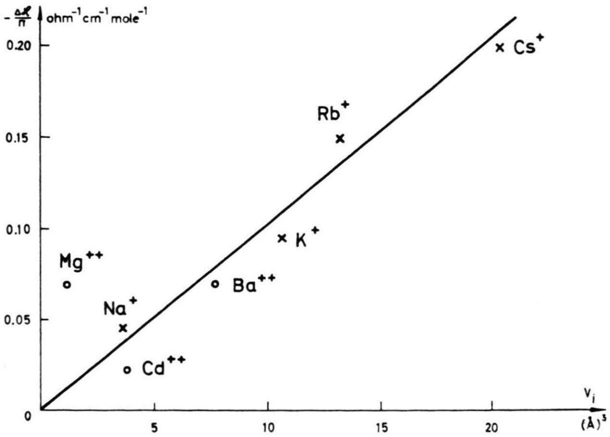

Fig. 2. The change in the electrical conductivity per mole per cent impurities as a function of the volume of the foreign cations at 890 °C.

the system $Li_2SO_4 - K_2SO_4$ shows volumetric additivity, and it is thus possible to calculate the densities at different concentrations from data given by JAEGER and KAHN [8].

There is an increase of the volume of the cations per mole of salt, but also a change in total molal volume, when a small quantity M_2SO_4 ($M = Na$, K, Rb, Cs) is added to molten lithium sulphate. If volumetric additivity is assumed for the mixtures with univalent cations the change in free volume ΔV_f can be calculated from the relation

$$\Delta V_f = \Delta V - \Delta V_i$$

where ΔV is the change in the molal volume and ΔV_i the change in the volume of the cations. Table 2 shows that the free volume is increasing with increasing size of the impurity cation and this increase thus seems to have little importance for the conductivity change in $(Li, M)_2SO_4$.

In Table 2 we have also tabulated the relative change of the equivalent electrical conductivity obtained from

$$\Delta\Lambda/\Lambda = \Delta V/V + \Delta\varkappa/\varkappa .$$

The external mobility of the nitrate ion is approximately constant in different nitrate mixtures [9] and we have assumed that this is valid also for the sulphate ion in the studied sulphate mixtures.

When a small quantity of M_2SO_4 is added to molten Li_2SO_4, then mean mobility of the Li^+ ions decreases. If the number of M^+ ions is so small that there is no interaction between them and if it is assumed that the ions are moving in groups, a few groups will contain one M^+ ion and some Li^+ ions. We now assume that these Li^+ ions have the same mobility as the M^+ ions and the rest of the Li^+ ions have the same mobility as the Li^+ ions in pure lithium sulphate. The number of Li^+ ions whose mobility has decreased is thus comparably small and it is possible to calculate the mean value of the number of cations in a group from the following relations.

The equivalent conductivity of a pure salt can be written

$$\Lambda_0 = F\, b_0$$

where F is the FARADAY constant and b_0 the mobility of the cation relative to the anion.

If we make use of the assumptions above, we can write for a mixure of Li_2SO_4 and 1 mole% M_2SO_4

$$\Lambda_1 = (F/100)\big((100-k)\, b_{Li^+} + k\, b_{M^+}\big)$$

where k is the number of ions taking part in a cooperative motion, $b_{Li^+} = b_0$ and b_{M^+} is the mobility of a group containing a M^+ ion.

This gives

$$\begin{aligned} \Delta\Lambda = \Lambda_0 - \Lambda_1 &= (F/100)\, k\, (b_{Li^+} - b_{M^+}) \\ &= (F/100)\, k\, \Delta b \\ \text{and } k &= 100\, (\Delta\Lambda/\Lambda)\, (b/\Delta b) . \end{aligned} \qquad (1)$$

The only sulphate system in which $\Delta b/b$ has been measured is $(Li, K)_2SO_4$ (loc. cit. [10]). We have calculated k of this system by extrapolating the mobility of the potassium ion to concentration zero. This gives $k = 2.7$, a value which should be compared with $k = 2.0$ for solid Li_2SO_4 calculated from the difference in mobility of the two lithium isotopes [11].

An interesting consequence of the higher k-value in the melt is that the isotope effect should be lower in the melt than in the solid. This is in agreement with observations made by LJUBIMOV and LUNDÉN [10] in $Li_2SO_4 - K_2SO_4$.

Salt	V cm³/mole	V_1 cm³/mole	ΔV cm³/mole	ΔV_i cm³/mole	ΔV_f cm³/mole	$\frac{\Delta V \cdot 10^2}{V(Li_2SO_4)}$	$-\frac{\Delta\varkappa\, 10^2}{\varkappa}$	$-\frac{\Delta\Lambda \cdot 10^2}{\Lambda}$
Li_2SO_4	55.20	—	—	—	—	—	—	—
Na_2SO_4	68.76	55.34	0.14	0.03	0.11	0.25	1.04	0.79
K_2SO_4	87.74	55.53	0.33	0.10	0.23	0.60	2.45	1.85
Rb_2SO_4	100.09	55.65	0.45	0.15	0.30	0.82	3.46	2.64
Cs_2SO_4	115.62	55.80	0.60	0.24	0.36	1.09	4.59	3.50

Table 2. The change of the free volume (ΔV_f) and the relative change of the equivalent conductivity ($\Delta\Lambda/\Lambda$) when 1 mole% M_2SO_4 is added to pure Li_2SO_4. V is the molal volume of the pure salts and V_1 the molal volume of the mixtures. ΔV_i is the change of the volume of the cations and ΔV_f the change of the free volume when the two salts are mixed

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For divalent impurity ions Eq. (1) can be written when we add 1 mole% MSO_4

$$k = 100(\Delta\Lambda/\Lambda)(b/\Delta b) - \tfrac{1}{2}(b/\Delta b).$$

If we assume that the number of ions taking part in a cooperative motion in molten lithium sulphate in not influenced by the foreign cation, it is possible to calculate the mobility of the impurity ion (Table 3). $\Delta b/b$ increases with increasing size of the foreign ion and with Cs^+ $\Delta b/b$ even exceeds one. It seems therefore probable that k increases somewhat with increasing size of the impurity ions. In molten metals it has been proposed that 3.3 atoms are moving in phase, a value which seems to be in resonable agreement with our results [12].

Ion	Na^+	K^+	Rb^+	Cs^+
$\Delta b/b$	0.27	0.64	0.91	1.21

Table 3. The relative mobility of the M^+ ion in molten Li_2SO_4 calculated from Eq. (1). It is assumed that $\Delta b/b$ is independent of temperature.

Since the densities of $BaSO_4$ and $CdSO_4$ are unknown, it is only possible to make a very rough estimation of $\Delta b/b$ of lithium sulphate with these salts. With $BaSO_4$ $\Delta b/b$ is less than 0.1 and with $CdSO_4$ about 0.4. The difference in mobility between the Ba^{++} and the Li^+ ions should thus be very small, but there is also a possibility that the mobility of the Li^+ ion is higher in $(Li_2, Ba)SO_4$ than in pure lithium sulphate due to the formation of vacancies in the pseudo-lattice (WAGNER effect).

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