# The Electrical Conductivity of the Solid and Molten System $Li_2SO_4$–$Na_2SO_4$

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The electrical conductivity of the solid and molten system $Li_2SO_4$-$Na_2SO_4$ has been measured at different concentrations. The relative excess conductivities for the systems $Li_2SO_4$-$Na_2SO_4$ and $Li_2SO_4$-$Ag_2SO_4$ were found to be identical and are decreasing with increasing temperature.

In our investigations of electrical conductivities of solid and molten sulphates[1–8], we have now measured the electrical conductivity of the system $Li_2SO_4$—$Na_2SO_4$. Since a high temperature modification is formed in nearly equimolar $Li_2SO_4$—$Na_2SO_4$, this system is interesting. The phase diagram has recently[9] been published.

The experimental technique described previously has been used with small modifications[5].

Measurements have been performed at 13 different concentrations (Table 1). The scattering in the results for the different concentrations is in this system somewhat larger than for instance for $Li_2SO_4$—$Ag_2SO_4$ due to corrosion of the cells by the sodium ions. Especially the mixtures are corrosive.

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-1})$ |
|---|---|
| 10 mole% $Na_2SO_4$ | |
| 1032.0 | 4.491 |
| 1022.5 | 4.485 |
| 1013.3 | 4.432 |
| 990.3 | 4.342 |
| 970.0 | 4.238 |
| 951.0 | 4.156 |
| 907.3 | 3.929 |
| 889.3 | 3.852 |
| 883.6 | 3.825 |
| 865.5 | 3.729 |
| 850.3 | 3.656 |
| 833.3 | 3.565 |
| 816.3 | 3.477 |
| 754.5 | 2.331 |
| 744.0 | 2.262 |
| 726.8 | 2.142 |
| 717.0 | 2.065 |
| 701.0 | 1.945 |
| 687.8 | 1.845 |
| 675.6 | 1.761 |
| 626.5 | 1.408 |
| 620.6 | 1.368 |
| 609.4 | 1.289 |
| 593.3 | 1.172 |
| 577.0 | 1.073 |
| 554.3 | 0.924 |
| 548.3 | 0.884 |
| 499.6 | 0.180 |
| 493.8 | 0.152 |
| 466.0 | 0.116 |
| 20 mole% $Na_2SO_4$ | |
| 940.5 | 3.622 |
| 924.2 | 3.567 |
| 901.0 | 3.463 |
| 838.2 | 3.138 |
| 819.5 | 3.036 |

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-1})$ |
|---|---|
| 787.6 | 2.887 |
| 768.5 | 2.778 |
| 739.8 | 2.625 |
| 715.8 | 2.485 |
| 686.7 | 1.841 |
| 659.4 | 1.590 |
| 632.0 | 1.431 |
| 567.0 | 1.063 |
| 549.6 | 0.955 |
| 518.0 | 0.770 |
| 493.7 | 0.646 |
| 30 mole% $Na_2SO_4$ | |
| 905.0 | 3.192 |
| 785.0 | 2.637 |
| 766.0 | 2.543 |
| 751.8 | 2.473 |
| 727.0 | 2.348 |
| 725.0 | 2.328 |
| 695.2 | 2.172 |
| 650.0 | 1.923 |
| 631.2 | 1.513 |
| 625.5 | 1.370 |
| 615.8 | 1.312 |
| 603.0 | 1.236 |
| 586.4 | 1.138 |
| 546.8 | 0.922 |
| 537.5 | 0.876 |
| 517.2 | 0.769 |
| 503.0 | 0.696 |
| 484.0 | 0.386 |
| 474.8 | 0.283 |
| 40 mole% $Na_2SO_4$ | |
| 783.8 | 2.459 |
| 767.0 | 2.379 |
| 750.5 | 2.310 |
| 738.8 | 2.249 |

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-1})$ |
|---|---|
| 723.0 | 2.164 |
| 694.8 | 2.017 |
| 679.8 | 1.941 |
| 666.0 | 1.867 |
| 647.8 | 1.769 |
| 637.2 | 1.706 |
| 627.8 | 1.653 |
| 620.2 | 1.620 |
| 609.4 | 1.545 |
| 602.2 | 1.512 |
| 591.8 | 1.336 |
| 579.6 | 1.231 |
| 565.5 | 1.146 |
| 549.8 | 1.044 |
| 542.2 | 0.994 |
| 527.5 | 0.909 |
| 500.0 | 0.085 |
| 490.0 | 0.045 |
| 50 mole% $Na_2SO_4$ | |
| 795.2 | 2.352 |
| 759.0 | 2.188 |
| 731.0 | 2.048 |
| 717.8 | 1.997 |
| 704.4 | 1.929 |
| 688.2 | 1.846 |
| 671.5 | 1.767 |
| 657.5 | 1.690 |
| 643.5 | 1.622 |
| 636.2 | 1.588 |
| 631.2 | 1.553 |
| 620.8 | 1.500 |
| 611.5 | 1.350 |
| 602.8 | 1.262 |
| 588.8 | 1.169 |
| 578.8 | 1.107 |
| 571.2 | 1.060 |
| 562.8 | 1.008 |
| 561.5 | 1.000 |

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-1})$ |
|---|---|
| 558.2 | 0.981 |
| 548.5 | 0.919 |
| 539.0 | 0.868 |
| 530.4 | 0.817 |
| 526.8 | 0.800 |
| 60 mole% $Na_2SO_4$ | |
| 893.5 | 2.553 |
| 881.2 | 2.512 |
| 865.8 | 2.448 |
| 850.2 | 2.376 |
| 833.0 | 2.313 |
| 828.8 | 2.298 |
| 818.5 | 2.260 |
| 789.2 | 2.139 |
| 770.5 | 2.058 |
| 754.2 | 1.994 |
| 738.5 | 1.914 |
| 714.0 | 1.807 |
| 693.2 | 1.720 |
| 692.0 | 1.713 |
| 672.8 | 1.612 |
| 657.2 | 1.540 |
| 641.8 | 1.465 |
| 624.6 | 1.249 |
| 620.8 | 1.212 |
| 613.5 | 1.103 |
| 607.5 | 0.991 |
| 597.2 | 0.819 |
| 586.8 | 0.657 |
| 576.2 | 0.528 |
| 571.6 | 0.453 |
| 559.5 | 0.396 |
| 557.6 | 0.3888 |
| 552.8 | 0.3728 |
| 544.2 | 0.3437 |
| 534.4 | 0.3109 |
| 525.2 | 0.2822 |

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-1})$ |
|---|---|
| 514.5 | 0.2527 |
| 505.8 | 0.0704 |
| 500.8 | 0.0391 |
| 497.8 | 0.0275 |
| 70 mole% $Na_2SO_4$ | |
| 999.0 | 3.593 |
| 987.3 | 3.536 |
| 977.0 | 3.497 |
| 958.0 | 3.426 |
| 947.0 | 3.376 |
| 911.0 | 3.225 |
| 897.0 | 3.184 |
| 851.5 | 2.966 |
| 828.8 | 2.877 |
| 812.3 | 2.807 |
| 796.8 | 2.710 |
| 772.0 | 2.590 |
| 730.2 | 2.359 |
| 721.8 | 2.330 |
| 701.3 | 2.223 |
| 687.5 | 2.130 |
| 653.3 | 1.935 |
| 640.5 | 1.811 |
| 629.0 | 1.580 |
| 615.8 | 1.330 |
| 597.6 | 1.211 |
| 577.0 | 1.095 |
| 558.8 | 0.991 |
| 545.0 | 0.920 |
| 497.8 | 0.628 |
| 490.3 | 0.513 |
| 80 mole% $Na_2SO_4$ | |
| 1065.0 | 2.900 |
| 1031.0 | 2.819 |
| 964.2 | 2.610 |

| $t$ (°C) | $\varkappa$ $(\Omega^{-1}\mathrm{cm}^{-3})$ |
|---|---|
| 911.5 | 2.433 |
| 866.2 | 2.289 |
| 848.2 | 2.217 |
| 837.5 | 2.178 |
| 811.2 | 2.078 |
| 765.2 | 1.898 |
| 719.7 | 0.810 |
| 695.2 | 0.477 |
| 671.5 | 0.391 |
| 634.7 | 0.282 |
| 90 mole% $Na_2SO_4$ | |
| 980.3 | 2.653 |
| 922.0 | 2.488 |
| 906.5 | 2.425 |
| 898.8 | 2.410 |
| 871.5 | 2.296 |
| 864.3 | 2.276 |
| 863.8 | 2.266 |
| 827.5 | 2.154 |
| 801.5 | 1.340 |
| 777.3 | 0.574 |
| 100 mole% $Na_2SO_4$ | |
| 1067.5 | 2.791 |
| 1053.0 | 2.754 |
| 1029.0 | 2.676 |
| 995.3 | 2.597 |
| 959.3 | 2.496 |
| 919.8 | 2.378 |
| 889.8 | 2.264 |
| 879.3 | 0.2457 |
| 863.0 | 0.1789 |
| 848.0 | 0.1335 |
| 834.5 | 0.1037 |
| 823.5 | 0.08444 |
| 820.3 | 0.07953 |

Table 1. The obtained conductivity results for the solid and molten system $Li_2SO_4$-$Na_2SO_4$.

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[1] A. KVIST and A. LUNDÉN, Z. Naturforsch. **20 a**, 235 [1965].

[2] A. KVIST, Z. Naturforsch. **21 a**, 487 [1966].

[3] A. KVIST, Z. Naturforsch. **21 a**, 1221 [1966].

[4] A. KVIST, Z. Naturforsch. **21 a**, 1601 [1966].

[5] A. KVIST, Z. Naturforsch. **22 a**, 208 [1967].

[6] A. KVIST, Z. Naturforsch. **22 a**, 467 [1967].

[7] A. KVIST and U. TROLLE, Z. Naturforsch. **22 a**, 1633 [1967].

[8] A. KVIST and K. SCHROEDER, Z. Naturforsch. **23 a**, 676 [1968].

[9] K. SCHROEDER and K. KVIST, Z. Naturforsch. **23 a**, 773 [1968].

*The molten state*

The maximal deviation from additivity for the molar volumes in molten $Li_2SO_4-Na_2SO_4$ is only 0.4% (l.c. 8) and the system can thus be considered ideal. The obtained equations for the molar conductivities are tabulated in Table 2. The specific conductivities for pure lithium and sodium sulphate have been published previously[2, 6], which also is the case for the mixtures with 2.0 and 4.9 mole% $Na_2SO_4$ (l.c. [10]). Since it is possible to discuss the conductivities starting from different models, they are given both in linear and exponential form in the table.

| mole% $Na_2SO_4$ | $a$ | $-b$ | $s_1$ | $Q$ | $\Lambda_0$ | $s_2$ | temperat. interval (°C) |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.34924 | 71.4 | 0.4 | 3930 | 1312 | 0.4 | 866–930 |
| 2.0 | 0.34868 | 73.3 | 0.3 | 3942 | 1306 | 0.3 | 867–917 |
| 4.9 | 0.32639 | 65.9 | 0.1 | 3885 | 1207 | 0.1 | 843–909 |
| 10.0 | 0.32248 | 69.0 | 0.3 | 4008 | 1237 | 0.3 | 816–1023 |
| 20.0 | 0.32646 | 93.9 | 0.6 | 4479 | 1368 | 0.6 | 716–941 |
| 30.0 | 0.31265 | 92.8 | 0.4 | 4580 | 1349 | 0.6 | 695–905 |
| 40.0 | 0.32918 | 111.3 | 0.4 | 5274 | 1822 | 0.8 | 602–784 |
| 50.0 | 0.31648 | 108.2 | 0.3 | 5303 | 1758 | 0.6 | 621–795 |
| 60.0 | 0.29091 | 97.4 | 0.5 | 5044 | 1441 | 0.9 | 642–894 |
| 70.0 | 0.32135 | 83.3 | 0.7 | 4272 | 1289 | 0.7 | 772–999 |
| 80.0 | 0.25488 | 71.4 | 0.9 | 4456 | 1071 | 0.8 | 765–1065 |
| 90.0 | 0.25988 | 71.8 | 0.7 | 4397 | 1070 | 0.7 | 828–980 |
| 100.0 | 0.25851 | 73.4 | 0.1 | 4441 | 1070 | 0.1 | 916–959 |

Table 2. The molar electrical conductivities of the molten system $Li_2SO_4$-$Na_2SO_4$ described by the relations $\Lambda = at + b$, where $t$ is the temperature in °C, and $\Lambda = \Lambda_0 \exp(-Q/RT)$, where $Q$ is the Arrhenius activation energy, $R$ the gas constant and $T$ the temperature in °K. $s$ is the standard deviation.

The system behaves as other systems normally do, if the Arrhenius activation energy ($Q$) is considered, i.e. $Q$ is higher in the mixtures than in the pure salts.

In a paper two years ago[5] we have proposed a model for the transport mechanism in molten salts, where we assumed that the ions are moving in groups, each group containing several anions and cations. It was then also possible to estimate the number of cooperating ions from a rather rough model.

The ionic radii of the sodium and silver ions are almost equal, about 0.95 Å, which leads to a very small excess conductivity in mixtures between a sodium and a silver salt with a common anion. The relative excess conductivities for the systems $Li_2SO_4-Ag_2SO_4$ and $Li_2SO_4-Na_2SO_4$ are found to be identical, and this supports the idea that the conductivity excess only is caused by differences in the ionic radii between the cations. This can also be seen for the two systems $Rb_2SO_4-Tl_2SO_4$ and $RbNO_3-TlNO_3$ (l.c. [11]).

When the temperature increases, there should be a decrease in the coupling between the different ions and as is seen in Fig. 1 the relative excess conductivity decreases. This thus means that the number of cooperating ions

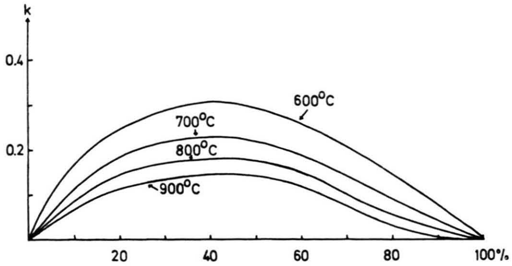

Fig. 1. The relative excess conductivity ($k$) as a function of the $Me^+$ concentration, $Me^+ = Na^+$ or $Ag^+$, for the system $Li_2SO_4$-$Me_2SO_4$.

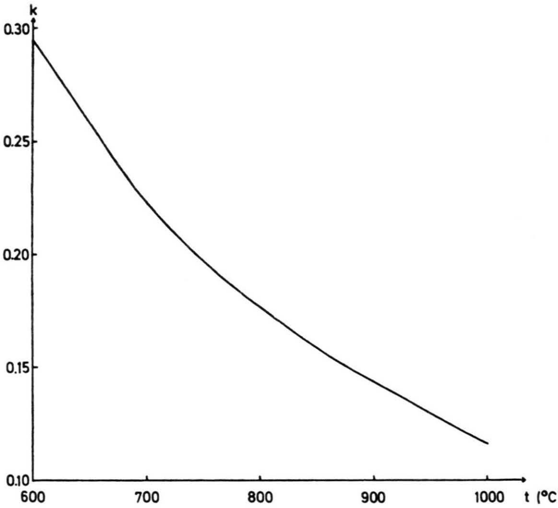

Fig. 2. The relative excess conductivity ($k$) as a function of the temperature for equimolar mixtures of $Li_2SO_4$ with $Me_2SO_4$, where Me = Na or Ag.

| mole% $Na_2SO_4$ | $Q$ (cal/mole) | $\varkappa_0$ ($\Omega^{-1}$ cm$^{-1}$) | $s$ ($\Omega^{-1}$ cm$^{-1}$) |
|---|---|---|---|
| | | fcc | |
| 0.0 | 9010 | 189.1 | 0.12 |
| 2.0 | 8390 | 142.4 | 0.04 |
| 4.9 | 8310 | 131.2 | 0.02 |
| 10.0 | 7860 | 112.3 | 0.03 |
| 20.0 | 8710 | 197.0 | 0.01 |
| 30.0 | 7630 | 99.7 | 0.01 |
| 40.0 | 8100 | 147.9 | 0.01 |
| | | bcc | |
| 40.0 | 8350 | 172.3 | 0.01 |
| 50.0 | 8390 | 157.5 | 0.01 |
| | | hexagonal | |
| 70.0 | 7500 | 93.0 | 0.002 |
| 80.0 | 15140 | 1255 | 0.001 |
| 90.0 | 22050 | 16340 | 0.006 |
| 100.0 | 46520 | $1694 \cdot 10^5$ | 0.002 |
| 100.0 | 47660 | $2692 \cdot 10^5$ | 0.002 |

Table 3. The specific electrical conductivities of the solid system $Li_2SO_4$-$Na_2SO_4$ described by the equation $\varkappa = \varkappa_0 \exp(-Q/RT)$. $s$ is standard deviation of $\varkappa$.

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[10] A. Kvist, Thesis, Göteborg 1967.

[11] V. Wagner and S. Forcheri, Z. Naturforsch. **22 a**, 891 [1967].

decreases with the temperature, but the temperature dependence of the excess change seems to be smaller at higher temperatures. It is probably not possible to experimentally find the temperature at which the excess is zero (Fig. 2).

It is possible to use our previous model for a calculation of the number of cooperating ions, but no conclusions can at present be drawn from this approximation.

### *The solid state*

There are three phases of particular interest, the f.c.c. phase in pure $Li_2SO_4$ and in mixtures with up to 40 mole% $Na_2SO_4$, the b.c.c. phase with 40 to 60 mole% $Na_2SO_4$ and the hexagonal phase with 60 to 100 mole% $Na_2SO_4$ (l.c.[9]).

The transformation temperatures obtained from the conductivity experiments are in good agreement with the DTA results. For the three pure phases equations are given in Table 3. In the f.c.c. and b.c.c. phases, the activation energies are almost equal, about 8.4 kcal/mole. In the hexagonal phase, $Q$ decreases when the lithium sulphate and also the disorder concentration increases. The diffusion coefficient of $Na^+$ in pure $Li_2SO_4$ has recently been determined[12] and diffusion experiments in lithium sulphate with different concentrations of sodium sulphate are in progress. A discussion of the transport mechanisms must therefore wait until the diffusion measurements are finished (l.c.[13]).

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[12] A. Kvist and A. Bengtzelius, Z. Naturforsch. **23a**, 679 [1968].

[13] A. Bengtzelius and A. Kvist, unpublished.

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## Diffusion in Cubic Sulphates

### IV. $^{22}Na$ and $^{24}Na$ in f.c.c. $Li_2SO_4$

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Simultanous diffusion of $^{22}Na^+$ and $^{24}Na^+$ in cubic lithium sulphate has been studied. The relative difference in diffusion coefficients for the two ions is $(2.8 \pm 0.4)\%$. The results are compared with previously obtained values for the $^6Li$ and $^7Li$ mobilities in lithium sulphate.

Some years ago Lundén[1] measured the relative mobility of the $^6Li^+$ and $^7Li^+$ ions in cubic lithium sulphate of natural composition and also the electrical conductivities of $^6Li_2SO_4$ and $^7Li_2SO_4$ have been studied[2]. The obtained relative differences in mobilities ($b$) were 2.1 and 4.2%, respectively. These values are lower than expected from a simple inverse mass root relation for the mobilities. The difference between $\Delta b/b$ for the isotopic pure salts and the mixture can easily be explained by assuming a cooperative transport model for the cations, where two ions are cooperating.

In a recent paper[3] we have reported on diffusion measurements of $Na^+$ ions in pure lithium sulphate and we have assumed that the same mechanism is responsible for the lithium and sodium ion transport[4]. This might, however, be confirmed by measuring the difference in diffusion coefficient of $^{22}Na^+$ and $^{24}Na^+$ in lithium sulphate.

The experimental technique has mainly been described elsewhere[5]. The surface layer contained $^{22}Na^+$ and $^{24}Na^+$ of about the same radioactive strength. Gamma ray spectra were obtained by using a NaI(Tl)-crystal coupled to a multichannel analyzer. In the spectra, the intensity of the 0.54 MeV and 2.75 MeV peaks were compared and it was then possible to calculate $\Delta D/D$ by comparing the intensities with the spectrum of pure $^{24}Na$. The experimental time was generally between two and three hours.

| Temperature (°C) | $\Delta D/D$ (%) |
|---|---|
| 694 | 3.1 |
| 721 | 2.7 |
| 730 | 3.2 |
| 771 | 2.9 |
| 774 | 2.5 |
| 776 | 2.3 |

Table 1. The relative difference between the diffusion coefficients of $^{22}Na^+$ and $^{24}Na^+$ in cubic lithium sulphate.

The results are given in Table 1. No definite temperature dependence of the difference can be found from these measurements. The mean valueof $\Delta D/D$ is $(2.8 \pm 0.4)$ % with the higher diffusion coefficient for $^{22}Na^+$.

For two isotopes, one generally uses the relation

$$b_1/b_2 - 1 = -f\,\Delta K\left((m_1/m_2)^{1/2} - 1\right),$$

where $m_i$ is the mass of the ion, $f$ a correlation factor and $\Delta K$ has been related to the share of the kinetic energy at the diffusive saddle point, which is associated with the diffusing ion rather than the surroundings[6].

For small isotope differences we obtain in our case with $f = 1$:

$$\Delta K = 2(\Delta D/D)/(\Delta m/m).$$

For $^{22}Na^+$ and $^{24}Na^+$ $\Delta K_{Na} = 0.64$ and this value should be compared, not with the electromigration value, but with the conductivity results[2], which gave $\Delta K_{Li'} = 0.55$. The two $\Delta K$ values are in fair agreement, but the results support our previous transport model, where the ions mainly are diffusing between the octahedral positions in the lattice.

This work was financially supported by the Swedish Council for Applied Research. Thanks are due to Dr. L. Broman for stimulating discussions.

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[1] A. Lundén, Z. Naturforsch. **17a**, 142 [1962].

[2] A. Kvist, Z. Naturforsch. **21a**, 487 [1966].

[3] A. Kvist and A. Bengtzelius, Z. Naturforsch. **23a**, 679 [1968].

[4] A. Kvist, A. Bengtzelius and U. Trolle, Z. Naturforsch. **23a**, 2042 [1968].

[5] L. Broman and K. Karlsson, Nucl. Instr. and Meth. **44**, 174 [1966].

[6] A. Lodding, Phys. Stat. Sol. **22**, 157 [1967].