

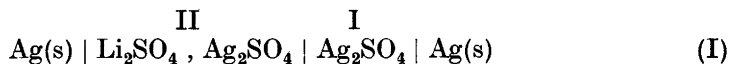
## Transport Properties in Solid and Liquid Mixtures of the System $\text{Li}_2\text{SO}_4\text{—Ag}_2\text{SO}_4$

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The  $\text{Li}_2\text{SO}_4\text{—Ag}_2\text{SO}_4$  system forms three different solid-solution phases at high temperature, each with a wide homogeneity range. The transport numbers of the solids have been determined as function of composition and temperature by a tracer technique. The relative transport numbers of the cations in the liquid mixtures have been evaluated along the liquidus line combining EMF values with known transport data for the solids, the phase diagram, and calorimetric data. The variation of the ionic mobilities with composition is discussed.

$\text{Li}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$  form quite unusual kinds of disordered solid mixtures as revealed by study of the concentration cell,<sup>1</sup>



and from X-ray diffraction studies of the solid phases.<sup>2</sup> The EMF for this cell is given in a convenient form by Førland<sup>3</sup>

$$\Delta E = -\frac{1}{F} \int_{\text{I}}^{\text{II}} \frac{t'_{\text{Li}^+}}{N_{\text{Li}^+}} d\mu_{\text{Ag}^+} \quad (\text{const } T) \quad (1a)$$

or defining

$$\Delta\psi = -F\Delta E = \int_{\text{I}}^{\text{II}} \frac{t'_{\text{Li}^+}}{N_{\text{Li}^+}} d\mu_{\text{Ag}^+} \quad (\text{const } T) \quad (1b)$$

$\mu_{\text{Ag}^+}$  is a shorthand notation for the chemical potential of half a mole  $\text{Ag}_2\text{SO}_4$ ,  $t'_{\text{Li}^+}$  denotes the electrochemical transport number relative to the  $\text{SO}_4^{2-}$ -ions,  $N_{\text{Li}^+}$  the ion fraction of  $\text{Li}^+$ ,  $F$  the Faraday constant and  $\Delta\psi$  represents then the difference in partial free enthalpy of  $\text{Ag}(\text{SO}_4)_{\frac{1}{2}}$  in the two half cells including the junction potential.

In order to interpret the EMF measurements in terms of the thermodynamic functions  $\Delta\mu_{\text{Ag}^+}$  and  $\Delta\bar{S}_{\text{Ag}^+}$  a knowledge of the transport properties of the solid solutions of  $\text{Li}_2\text{SO}_4\text{—Ag}_2\text{SO}_4$  is required.

When the thermodynamic properties of the solid mixtures are known, the thermodynamic properties of the molten mixtures can be calculated from the phase diagram. Then by comparing the measured EMF and the calculated  $\Delta\mu_{\text{Ag}^+}$ , eqn. (1b) can be used for calculation of the transport number  $t'_{\text{Ag}^+}$  in the molten mixtures.

A preliminary investigation of specific conductivity of  $\text{Li}_2\text{SO}_4$ ,  $\text{LiAgSO}_4$ , and  $\text{Ag}_2\text{SO}_4$  was also carried out in order to give a qualitative discussion of the ionic mobilities in this system.

The transport numbers of  $\text{Ag}^+$  in these solid solutions have previously been measured by Eide.<sup>4,2</sup> Due to experimental difficulties the results were not accurate enough for a reliable calculation of  $\Delta\mu_{\text{Ag}^+}$  and  $\Delta\bar{S}_{\text{Ag}^+}$  from eqn. (1b). Conclusions as to the change of  $t_{\text{Ag}^+}$  with temperature could not be drawn, except for the phase rich in  $\text{Li}_2\text{SO}_4$ , where a decrease of  $t_{\text{Ag}^+}$  with temperature was indicated.

In this investigation transport numbers were determined over the whole concentration range applying a method developed by Eide, Førland and Reitan.<sup>5</sup> The method was slightly modified in order to obtain more reliable results for mixtures with high contents of  $\text{Ag}_2\text{SO}_4$ .

Transport numbers in solid salts can be determined by two different methods:

a) The Hittorf method, where concentration changes in the cathode and anode compartments are measured. By this method only relative transport numbers can be evaluated, but this is sufficient for the determination of the junction potential.

b) The solid salt represents a reference frame for the movements of the ions. By a tracer technique it is possible to determine the absolute transport numbers of the ions.

The transport number of  $\text{Ag}^+$  in solid  $\text{Li}_2\text{SO}_4$ - $\text{Ag}_2\text{SO}_4$  was determined by method b). The anolyte contained the  $\gamma$ -active isotope  $^{110\text{m}}\text{Ag}$ . By an electrolysis between Ag electrodes the amount of  $^{110\text{m}}\text{Ag}^+$  transported into the catholyte was determined. The same technique was applied for the determination of  $t_{\text{SO}_4^{2-}}$  in solid  $\text{LiAgSO}_4$  utilizing the  $\beta$ -active isotope  $^{35}\text{S}$ .

An attempt to combine the tracer experiment with the Hittorf experiment was not successful. The Ag was deposited on the cathode as thin dendrites that grew throughout the cathodic mixture. Due to this dendrite formation, the amount of cathodic mixture to be analyzed will be large and the concentration change accordingly will be small.

## EXPERIMENTAL

*Experimental set-up.* The experimental arrangement is shown in Fig. 1a. The anode and cathode compartments were made of silica glass tubes. The anode tube ended in a thin capillary, 1 mm I. D., to reduce the diffusion and ease the separation of the two compartments after electrolysis.

The arrangement was slightly modified for compositions in the range 75–100 mole %  $\text{Ag}_2\text{SO}_4$ , (Fig. 1b). In this range very thin silver dendrites grew out from the cathode during the electrolysis. The dendrites could reach the anodic mixture when less than 50 mg Ag was deposited, thus ruining the experiment. When the composition of the mixture was below 75 mole %, the dendrite growth was considerably reduced. The

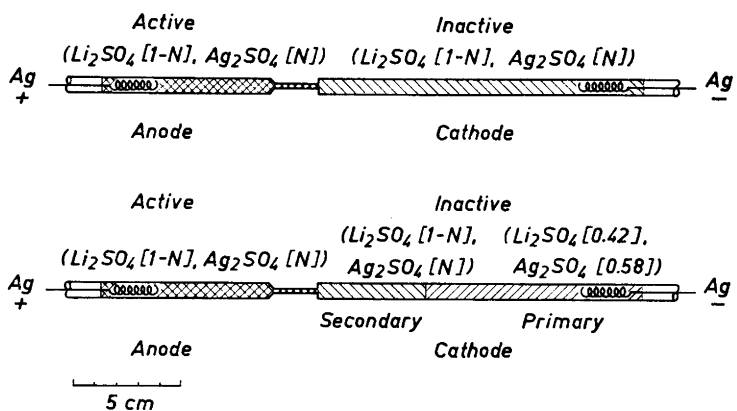


Fig. 1. Electrolyte cells for the determination of  $t_{Ag^+}$  in solid Li<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> mixtures.

- a) Experimental set-up for  $N_{Ag^+} < 0.75$ .  
 b) Experimental set-up for  $N_{Ag^+} > 0.75$ .

cathode compartment therefore was divided into two parts. A mixture of 58 mole % AgSO<sub>4</sub>\* was in contact with the Ag cathode to reduce the growth of the Ag dendrites. The secondary cathode tube contained the mixture for which the transport number was measured.

Attempts were made to reduce the growth of Ag dendrites in mixtures high in Ag<sub>2</sub>SO<sub>4</sub> by superimposing an alternating current on the direct current. This proved to be unsuccessful.

The furnace was a "general purpose laboratory furnace" used in the author's laboratory and described elsewhere.<sup>6</sup> The variation of the temperature was less than 2°C along the central 20 cm of the furnace tube. The temperature was kept constant within ±5°C.

The temperature was measured with a calibrated Pt/Pt-10Rh thermocouple. The direct current supply was a selenium rectifier with a variable resistor and a mA meter connected in series with the transport number cell. The amount of current that passed through the cell was measured with an Ag coulometer. (Ag was deposited on a Pt crucible from a 10% AgNO<sub>3</sub> solution.)

The amount of active <sup>110m</sup>Ag was measured by a scintillation counter connected with an automatic scaler. The annular sample method was applied in the measurements. An aqueous solution of a  $\gamma$ -active material is filled into a 10 ml polythene container. The container is so designed that the sample completely surrounds the tap-formed scintillation crystal.

**Chemicals.** The Li<sub>2</sub>SO<sub>4</sub> was Analar quality (Hopkin and Williams, Chadwell Heath, England). The Ag<sub>2</sub>SO<sub>4</sub> was a special quality Ag<sub>2</sub>SO<sub>4</sub> cryst. (Merck, Darmstadt, Germany). Max. limit of impurities 0.15%.

The Ag electrodes had a purity of 99.998% (Johnson and Matthey, Ltd., London, England). The isotope <sup>110m</sup>Ag mainly emits  $\gamma$ -radiation. It was delivered by the Institute for Atomic Energy, Lillestrøm, Norway, as metallic Ag, and converted to Ag<sub>2</sub>SO<sub>4</sub>. The  $\beta$ -active <sup>36</sup>S was delivered as SO<sub>4</sub><sup>2-</sup> in weak HCl by Oak Ridge National Laboratory, Oak Ridge, Tenn., USA.

**Procedure.** The radioactive AgSO<sub>4</sub> was mixed carefully with a large quantity of inactive Ag<sub>2</sub>SO<sub>4</sub> in the molten state to obtain a salt with suitable activity. The Ag<sub>2</sub>SO<sub>4</sub> used had an activity of about 700 counts/sec g.

\* The composition 58 mole % was chosen because the Li<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> has an eutectic at that composition.

The molten mixture of  $\text{Li}_2\text{SO}_4\text{--Ag}_2\text{SO}_4$  was sucked into the silica glass tubes. The tubes were left in the furnace overnight to smooth out concentration gradients. They were then pressed lightly against each other and the electrolysis was started.

The electrolysis current was usually kept at about 5 mA, but in some cases the current could be as low as 1 mA and as high as 7 mA. The applied voltage was between 12 and 150 V depending on the temperature and the composition of the mixture. Usually about 50mAh was sent through the cell.

A calculation showed the local heating of the  $\text{Li}_2\text{SO}_4\text{--Ag}_2\text{SO}_4$  mixture caused by the direct current applied in the electrolysis to be negligible.

The measured transport numbers were independent of the magnitude of the applied current (in the range 1–7 mA). The experiments were performed in the temperature range 693°K–933°K. Only homogeneous phases were investigated.

When the electrolysis was completed the cathodic mixture was dissolved in 10 % nitric acid and the total activity was determined. The specific activity of the cathodic mixture before the electrolysis was similarly determined in 10 % nitric acid solution. Two samples were taken from each solution. Every sample was counted three times, and at least 30 000 disintegrations were registered each time.

No corrections were necessary for absorption of radiation in the sample solution or for the "dead time" of the scintillation crystal.

Small differences in the geometry of the different polythene containers used for radioactive counting resulted in different countings. As the transport number of  $\text{Ag}^+$  is given as the quotient of two activities, however, this trouble was overcome by using the same container for both radioactive solutions.

The specific radioactivity of the mixture in the thin anodic tube in contact with the initially inactive cathodic mixture was determined after the electrolysis. Within the experimental error it was found to have the same specific activity as the rest of the radioactive mixture. This verifies that the thermal self-diffusion is negligible.

The amount of active  $\text{SO}_4^{2-}$  transported was determined by a separate experiment. The activity of  $^{35}\text{S}$  was determined by finely grinding the sample and suspending it in a scintillation counter solution.

#### TRANSPORT NUMBERS IN SOLID SOLUTIONS

It was expected that  $t_{\text{SO}_4^{2-}}$  was negligible compared to  $t_{\text{Ag}^+}$  and  $t_{\text{Li}^+}$  in solid solutions of  $\text{Li}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$ . The measured value  $t_{\text{Ag}^+} = 1$  in  $\alpha\text{-Ag}_2\text{SO}_4$  is an indication of this. Lundén<sup>7</sup> has found the transport number of  $\text{Li}^+$  ions in  $\alpha\text{-Li}_2\text{SO}_4$  equal to unity. In order to have a further check on this point a solid mixture of composition  $\text{LiAgSO}_4$  was chosen for investigation of  $t_{\text{SO}_4^{2-}}$ . At this composition a solid solution with cubic body-centered structure is formed between 731 and 845°K. This phase was the most disordered of the three phases and  $t_{\text{SO}_4^{2-}}$  was expected to be smaller in both the  $\alpha\text{-Li}_2\text{SO}_4$ -phase and the  $\alpha\text{-Ag}_2\text{SO}_4$ -phase.

The transport number  $t_{\text{SO}_4^{2-}}$  was established to be very small indeed in  $\text{LiAgSO}_4$  at 773°K, and an accurate determination was not possible. But it was established that  $t_{\text{SO}_4^{2-}} < 0.004$  which is less than the experimental error for the determination of  $t_{\text{Ag}^+}$ . Hence:  $t_{\text{Ag}^+}$  (relative to the bulk solid) =  $t'_{\text{Ag}^+}$  (relative to the  $\text{SO}_4^{2-}$  ions)

$$t_{\text{Li}^+} = t'_{\text{Li}^+} = 1 - t_{\text{Ag}^+} \quad (2)$$

The measured transport number  $t_{\text{Ag}^+}$  can then be used directly for calculation of  $\Delta\mu_{\text{Ag}^+}$  according to eqn. (1b).



tion is found to be  $\pm 0.5\%$ . From the results on Fig. 2 the total standard deviation of  $t_{\text{Ag}^+}$  is estimated to  $\pm 0.008$ .

The reason why  $t_{\text{Ag}^+}$  for two runs with 100 mole %  $\text{Ag}_2\text{SO}_4$  is 2.5 % above the highest theoretical value 1.000 is not known.

The results indicate variations of  $t_{\text{Ag}^+}$  with temperature. The temperature variations of  $t_{\text{Ag}^+}$  are estimated as follows:

$$\text{Phase I } (823^\circ\text{K} < T < 933^\circ\text{K}) : \frac{\partial t_{\text{Ag}^+}}{\partial T} = -2 \times 10^{-3} N_{\text{Ag}^+}$$

$$\text{Phase II } (693^\circ\text{K} < T < 823^\circ\text{K}) : \frac{\partial t_{\text{Ag}^+}}{\partial T} = 1.5 \times 10^{-4}$$

$$\text{Phase III } (693^\circ\text{K} < T < 823^\circ\text{K}) : \frac{\partial t_{\text{Ag}^+}}{\partial T} = 2 \times 10^{-3} (1 - N_{\text{Ag}^+})$$

The standard deviation of  $\partial t_{\text{Ag}^+}/\partial T$  was estimated to be  $9 \times 10^{-5}$  taking  $\Delta T$  as  $120^\circ\text{K}$ .

#### CALCULATION OF RELATIVE TRANSPORT NUMBERS IN MOLTEN MIXTURES

From the measured EMF for cell I and the measured transport numbers,  $\Delta\mu_{\text{Ag}^+}(\text{s})$  for the solid mixtures has been calculated from eqn. (1b) rearranged:<sup>1,2</sup>

$$\Delta\mu_{\text{Ag}^+} = \int_{\text{I}}^{\text{II}} \frac{N_{\text{Li}^+}}{t'_{\text{Li}^+}} d\psi_{\text{Ag}^+} \quad (\text{const } T) \quad (4)$$

The chemical potential of  $\text{Ag}^+$  in the molten mixtures,  $\Delta\mu_{\text{Ag}^+}(\text{l})$ , can be calculated from  $\Delta\mu_{\text{Ag}^+}(\text{s})$  by aid of the phase diagram. The chemical potential of half a mole  $\text{Ag}_2\text{SO}_4$  in the liquid mixture in equilibrium with the solid mixture is given by the equation:

$$\Delta\mu_{\text{Ag}^+}(\text{l}) = \Delta\mu_{\text{Ag}^+}(\text{s}) - \Delta H_{t_{\text{Ag}^+}}(1 - T/T_f) \quad (5)$$

$T_f$  is the melting point of pure  $\text{Ag}_2\text{SO}_4$  and  $\Delta H_{t_{\text{Ag}^+}}$  is one half of its enthalpy of fusion. The reference states for  $\Delta\mu_{\text{Ag}^+}(\text{l})$  and  $\Delta\mu_{\text{Ag}^+}(\text{s})$  are pure liquid  $\text{Ag}_2\text{SO}_4$  and pure solid  $\text{Ag}_2\text{SO}_4$ , respectively. The correction term due to the difference in heat capacity of solid and liquid  $\text{Ag}_2\text{SO}_4$  is considered of minor importance and has been neglected.

Combination of eqns. (4) and (5):

$$\frac{t'_{\text{Li}^+}(\text{l})}{N_{\text{Li}^+}} = \frac{d(\Delta\psi(\text{l}))}{d \left[ \int_{N_{\text{Ag}^+}=1}^{N_{\text{Ag}^+}=N} \left( \frac{N_{\text{Li}^+}}{t'_{\text{Li}^+}(\text{s})} \right) d\psi_{\text{Ag}^+}(\text{s}) - \Delta H_{t_{\text{Ag}^+}} (1 - T/T_f) \right]} \quad (\text{const } T) \quad (6)$$

From this equation  $t'_{\text{Li}^+}(\text{l})$  has been calculated along the liquidus line for  $0.818 < N_{\text{Ag}^+} < 1$  from measured values of  $\Delta\psi(\text{l})$ ,  $\Delta\psi(\text{s})$ ,  $t'_{\text{Li}^+}(\text{s})$  and  $\Delta H_{t_{\text{Ag}^+}} = 1.83 \text{ kcal/mole}$ .<sup>2</sup> The corresponding compositions on the liquidus and the solidus line at a certain temperature are given in the phase diagram.<sup>1</sup>

For  $0.35 < N_{\text{Ag}^+} < 0.818$  eqn. (6) is valid if  $\Delta H^*_{\text{fAg}^+}$  is substituted for  $\Delta H_{\text{fAg}^+}$ .  $H^*_{\text{fAg}^+}$  is the hypothetical heat of fusion of half a mole of pure  $\text{Ag}_2\text{SO}_4$  isomorphous with phase II. As both the heat of fusion for phase II ( $\Delta H_{\text{fLiAgSO}_4} = 0.41 \text{ kcal/mole}^2$ ) and the freezing point depression<sup>1</sup> are very small, the heat term in the denominator in eqn. (6) can be neglected, giving

$$\frac{t'_{\text{Li}^+}(\text{l})}{N_{\text{Li}^+}} = \frac{d(\Delta\psi(\text{l}))}{d \left[ \int_{N_{\text{Ag}^+} = 0.818}^{N_{\text{Ag}^+} = N} \frac{N_{\text{Li}^+}}{t'_{\text{Li}^+}(\text{s})} d\psi_{\text{Ag}^+}(\text{s}) \right]} \quad (7)$$

From this equation,  $t'_{\text{Li}^+}(\text{l})$  was calculated along the liquidus line in the range  $0.35 < N_{\text{Ag}^+} < 0.818$ .<sup>†</sup>

The calculations of  $t'_{\text{Li}^+}(\text{l})$  for  $0.818 < N_{\text{Ag}^+} < 1$  and for  $0.35 < N_{\text{Ag}^+} < 0.818$  are independent. The two ways of calculation lead to values of  $t'_{\text{Li}^+}(\text{l})$  for  $N_{\text{Ag}^+} = 0.818$  which differ by less than 2 %.

The results of the calculation for  $0.818 < N_{\text{Ag}^+} < 1$  and  $0.35 < N_{\text{Ag}^+} < 0.818$  are given as  $t'_{\text{Ag}^+}(\text{l}) = 1 - t'_{\text{Li}^+}(\text{l})$  on Fig. 2. The small difference found around  $N_{\text{Ag}^+} = 0.818$  has been smoothed out.

It is not possible to calculate  $t'_{\text{Li}^+}(\text{l})$  with sufficient accuracy for compositions with  $N_{\text{Ag}^+} < 0.35$ . Necessarily  $N_{\text{Li}^+}/t'_{\text{Li}^+} \rightarrow 1$  and  $\Delta\psi_{\text{Ag}^+} \rightarrow -\infty$  when  $N_{\text{Ag}^+} \rightarrow 0$ . This will tend to make the difference in  $\Delta\mu_{\text{Ag}^+}$  equal to the difference in  $\Delta\psi$  in this concentration range and hence make the measurements relative insensitive to variations in  $t'_{\text{Li}^+}/N_{\text{Li}^+}$ .

The results for  $0.35 < N_{\text{Ag}^+} < 1$  seem to indicate that  $t'_{\text{Ag}^+}(\text{l})$  become smaller than  $N_{\text{Ag}^+}$  in the concentration range  $0 < N_{\text{Ag}^+} < 0.35$ .

## DISCUSSION

The agreement with Eide's previous measurements<sup>4,2</sup> in this system is satisfactory taking into consideration that the precision of his measurements were lower than the present ones, due to experimental difficulties.

The main purpose of this study was to obtain transport numbers of sufficient accuracy to calculate the thermodynamic functions of the  $\text{Li}_2\text{SO}_4$ — $\text{Ag}_2\text{SO}_4$  mixtures from the study of the concentration cell I. For this purpose the obtained data has been sufficiently accurate, except in the  $\text{Ag}_2\text{SO}_4$ -rich phase III where only  $\Delta\mu_{\text{Ag}^+}$  and not  $\Delta\bar{S}_{\text{Ag}^+}$  could be calculated.  $\Delta\bar{S}_{\text{Ag}^+}$  is dependent both on the temperature coefficients of the EMF and  $t_{\text{Ag}^+}$ . In phase III the estimated deviation of  $\partial t_{\text{Ag}^+}/\partial T$  was too large to make a reliable calculation of  $\Delta\bar{S}_{\text{Ag}^+}$  possible. The results of the calculation of thermodynamic functions will be presented in a subsequent paper.

The transport properties of solid and liquid mixtures of  $\text{Li}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$  exhibit rather unusual features which deserve some comments.

<sup>†</sup>  $t'_{\text{Li}^+}(\text{l})$  may also be calculated with less accuracy from the "hump" discussed in a previous paper.<sup>1</sup>

A preliminary investigation of the specific conductance  $\kappa$  for  $\text{Li}_2\text{SO}_4$ ,  $\text{LiAgSO}_4$ , and  $\text{Ag}_2\text{SO}_4$  has been carried out.<sup>8</sup> (The AC-instrument available for this investigation did not permit extrapolation to infinite frequency or corrections for impedance in the circuit, and the results were hence considered to be semiquantitative only.) The measured values for  $\text{Li}_2\text{SO}_4$  and  $\text{LiAgSO}_4$  agree within 6 % with the more careful measurements by Førlund and Støren,<sup>9</sup> and by Kvist and Lundén.<sup>10</sup> All investigations revealed that the solid high-temperature phases exhibit electrical conductance more typical of a molten than a solid ionic salt. In the present work the following ratios of  $\kappa(l)/\kappa(s)$  was observed around the melting point: 1.10 for  $\text{LiAgSO}_4$ , 1.29 for  $\text{Li}_2\text{SO}_4$  and 6.5 for  $\text{Ag}_2\text{SO}_4$ . Even the latter ratio is small compared to that of  $\text{NaCl}$  where  $\kappa(l)/\kappa(s) = 5000$ .<sup>11,12</sup> At  $T = 1000^\circ\text{K}$  the specific conductance of  $\text{Li}_2\text{SO}_4(s)$ ,  $\text{LiAgSO}_4(s)$ , and  $\text{Ag}_2\text{SO}_4(l)$  all are about  $6 \Omega^{-1}\text{cm}^{-1}$ .

*Mobilities in solid mixtures.* The curves for  $t_{\text{Ag}^+}(s)$  at  $540^\circ\text{C}$  on Fig. 2 are drawn to the composition of the two-phase boundaries in the phase diagram. At this temperature mixtures in equilibrium are 20–35.5 mole %  $\text{Ag}_2\text{SO}_4$  (I–II) and 75–84.5 mole %  $\text{Ag}_2\text{SO}_4$  (II–III). Accidentally  $t_{\text{Ag}^+}$  is observed to be approximately the same for the phases in equilibrium.

When discussing the relative transport properties of  $\text{Ag}^+$  and  $\text{Li}^+$  ions it is useful to consider the ratio between the electrical mobilities given by

$$\frac{u_{\text{Ag}^+}}{u_{\text{Li}^+}} = \frac{t_{\text{Ag}^+}/N_{\text{Ag}^+}}{t_{\text{Li}^+}/N_{\text{Li}^+}} \quad (8)$$

The diagonal line on Fig. 2 corresponds to the mobilities of  $\text{Ag}^+$  and  $\text{Li}^+$  being equal.

In phase III which is the most ordered solid  $u_{\text{Ag}^+}(s)/u_{\text{Li}^+}(s) = 0.50$  at  $420^\circ\text{C}$  and  $0.86 < N_{\text{Ag}^+} < 1$ , but with increasing temperature the ratio  $u_{\text{Ag}^+}(s)/u_{\text{Li}^+}(s)$  increases rapidly (as well as the absolute values of the mobilities). In phase I below  $660^\circ\text{C}$  the opposite effect is noted,  $u_{\text{Ag}^+}(s)/u_{\text{Li}^+}(s) \approx 1.47$  at  $540^\circ\text{C}$  and  $0.10 < N_{\text{Ag}^+} < 0.20$  and this ratio decreases rapidly with temperature. It is hence demonstrated that in both these two structures the minority ion has the greatest mobility this effect being increased with decreasing temperature.

In phase II, the most disordered of the solids,  $u_{\text{Li}^+}(s) \approx u_{\text{Ag}^+}(s)$ ,  $u_{\text{Ag}^+}(s)$  being largest on the  $\text{Ag}_2\text{SO}_4$  side and  $u_{\text{Li}^+}(s)$  being largest on the  $\text{Li}_2\text{SO}_4$  side. In accordance with what is generally observed for melts, the temperature coefficient of the transport numbers is small, in this case  $t_{\text{Ag}^+}$  increases slightly with temperature for  $N_{\text{Ag}^+} = 0.60$ .

Increase of temperature tends to make the ratio  $u_{\text{Ag}^+}/u_{\text{Li}^+}$  for the solid phases to shift toward the values calculated for the liquid phase.

*Mobilities in liquid mixtures.* For the liquid mixtures the transport number  $t'_{\text{Ag}^+}(l)$  relative to the  $\text{SO}_4^{2-}$  ions has been calculated (Fig. 2). In the molten state it is not to be expected that  $t_{\text{SO}_4^{2-}}$  is negligible even if  $t_{\text{SO}_4^{2-}}(l)$  is considered to be small because of the double charge of the  $\text{SO}_4^{2-}$  ion.

For mixtures rich in  $\text{Ag}_2\text{SO}_4$   $u'_{\text{Ag}^+}(l)/u'_{\text{Li}^+}(l) = 1.4$  for  $0.7 < N_{\text{Ag}^+} < 1$ . From the shape of the  $t'_{\text{Ag}^+}(l)$  curve one would expect that  $u'_{\text{Ag}^+}(l)/u'_{\text{Li}^+}(l) < 1$  in mixtures rich on  $\text{Li}_2\text{SO}_4$ . These results are contrary to what is found



for the solid phases where the minority ion had the greatest mobility. The specific conductivity of molten Li<sub>2</sub>SO<sub>4</sub> extrapolated to 1000°K is about 75 % greater than that for molten Ag<sub>2</sub>SO<sub>4</sub>. Assuming  $t_{\text{SO}_4^{2-}}$  small or equal in the two salts  $u'_{\text{Ag}^+}(1)/u'_{\text{Li}^+}(1) = 0.57$  for the pure salts.

In mixtures rich in Ag<sub>2</sub>SO<sub>4</sub> a strong preference for the movement of Ag<sup>+</sup> ions relative to the Li<sup>+</sup> ions is observed in spite of the fact that  $u_{\text{Ag}^+}/u_{\text{Li}^+} < 1$  for the pure salts. In mixtures rich in Li<sub>2</sub>SO<sub>4</sub> the movement of Li<sup>+</sup> ions seems to be preferred.

These results conform to a fairly frequent observed phenomenon which is observed in the molten mixtures of LiCl—KCl,<sup>13</sup> LiBr—NaBr,<sup>14</sup> LiBr—KBr,<sup>14</sup> LiNO<sub>3</sub>—KNO<sub>3</sub>,<sup>15</sup> and NaNO<sub>3</sub>—KNO<sub>3</sub>.<sup>16</sup> In these systems a crossing of the relative cation mobilities is demonstrated, *i.e.*  $u_{\text{M}_1^+}/u_{\text{M}_2^+} \geq 1$  dependent on composition. The crossing is so as to make the mobility of the majority cation the largest in the nearly pure salt.

Various mechanisms have been proposed to account for this feature. Perie *et al.*<sup>14</sup> have suggested formation of ion groups entrapping one of the cations, while Moynihan and Laity<sup>13</sup> have discussed the transport properties of Li<sup>+</sup> and K<sup>+</sup> in molten LiCl—KCl as due to the change in the polarization of the anions.<sup>17</sup> The Li<sup>+</sup> ions have a greater ability to polarize the Cl<sup>−</sup> ions, which will tend to strengthen the Li<sup>+</sup>—Cl<sup>−</sup> bond and weaken the K<sup>+</sup>—Cl<sup>−</sup> bond. The Li<sup>+</sup>—Cl<sup>−</sup> bond is hence expected to be stronger in KCl than in LiCl. This may explain the lowering of Li<sup>+</sup> mobility in mixtures rich in KCl, and the observed crossover of mobilities at an intermediate composition.

The system Li<sub>2</sub>SO<sub>4</sub>—Ag<sub>2</sub>SO<sub>4</sub> exhibits a positive enthalpy of mixing and a positive deviation from ideal solution and is thus different from the systems mentioned above. As coulombic and polarizing forces are expected to give rise to a negative enthalpy of mixing, the positive excess enthalpy can be considered due to change in the van der Waals forces. It is still possible, however, that the transport properties are determined by the change in polarizing forces even if the van der Waals forces are the energetically dominant excess force.

A discussion of transport properties from a force concept related to thermodynamics may well be deceptive, however, especially in mixtures with a large non-centrosymmetrical anion like the SO<sub>4</sub><sup>2−</sup> group. In the sulphate system the movements of the cations can be strongly coupled to the rotation and vibration of the sulphate groups, the movements of these groups being different in molten Li<sub>2</sub>SO<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub>. Further studies of conductivity, density and self-diffusion are needed to shed more light upon the type of mechanism being predominant.

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