schen Leitfähigkeit von Benzol nicht miteinander übereinstimmen. Da selbst Elektroden aus gleichem Material beim Umpolen der Spannung ein unterschiedliches elektrisches Verhalten zeigten, ist es sehr wahrscheinlich, daß sich die Vorgänge, die die Größe des elektrischen Stromes in flüssigem Benzol bestimmen, an der Phasengrenze Elektrode – Benzol abspielen und sehr empfindlich auf Unterschiede im Zustand der Elektrodenoberfläche reagieren. Es ist also nicht möglich, aus solchen Messungen die spezifische elektrische Leitfähigkeit von flüssigem Benzol zu ermitteln.

The Electrical Conductivity of the Molten System $(Li,K)_2(SO_4,WO_4)$

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The electrical conductivities of molten Li_2SO_4, Li_2WO_4, K_2SO_4, K_2WO_4 and their equimolar mixtures have been measured up to 1100 °C. The equivalent conductivities and the ARRHENIUS activation energies indicate that the transport mechanism is mainly determined by the cations.

One of the authors has recently found [1] that the molar electrical conductivity (Λ) of $LiKSO_4$ is considerably lower than Λ of pure Li_2SO_4 and K_2SO_4, while the conductivity of equimolar $Li_2SO_4-Li_2WO_4$, where $\Lambda(Li_2WO_4) \approx \Lambda(K_2SO_4)$, is almost ideal. The anions thus seem to have little importance for the conduction mechanism in such melts. We therefore found it interesting to compare the conductivities of Li_2SO_4, Li_2WO_4, K_2SO_4 and K_2WO_4 with their equimolar mixtures.

The experimental technique is described elsewhere in detail [2]. The salts, Li_2SO_4 (Hopkin & Williams AnalaR), K_2SO_4 (Merck p. a.), Li_2WO_4 (Hopkin & Williams) and K_2WO_4 (Hopkin & Williams), were used without further purification.

The specific conductivities ($\varkappa$) of K_2WO_4, $K_2SO_4-K_2WO_4$, $Li_2WO_4-K_2WO_4$ and $Li_2SO_4-K_2WO_4$ are given in Table 1. The conductivity of K_2WO_4 agrees within 1% with results obtained by MORRIS and ROBINSON [3].

$\varkappa$ and Λ of Li_2SO_4, $Li_2SO_4-K_2SO_4$, $Li_2SO_4-Li_2WO_4$ and Li_2WO_4 have recently been published (l. c. [1, 3, 4–6]).

The molar conductivities were calculated by assuming volumetric additivity of the salts. The densities were obtained from MORRIS and ROBINSON [3], JAEGER and KAHN [7] and KVIST [2]. The volumetric additivity was checked by comparing the mean value of the molar volumes of Li_2SO_4 and K_2WO_4 (V_1) with that of Li_2WO_4 and K_2SO_4 (V_2). A difference of about 4% was found, but this difference is neglectable in this case. The molar volume of $LiK(SO_4WO_4)_{1/2}$ was taken as the mean value of V_1 and V_2.

Linear equations for Λ are given in Table 2.

t (°C)	$\varkappa$ (Ω^{-1} cm^{-1})	t (°C)	$\varkappa$ (Ω^{-1} cm^{-1})
K_2WO_4		$LiKWO_4$	
1036.2	1.351	918.0	1.123
1035.8	1.351	912.5	1.108
1026.2	1.333	902.2	1.083
1004.2	1.300	888.0	1.045
1003.0	1.296	858.0	0.971
1000.8	1.292	845.2	0.938
991.0	1.272	814.2	0.861
974.2	1.242	796.0	0.816
954.8	1.207	781.8	0.781
933.0	1.155	752.2	0.705
		733.8	0.658
		716.8	0.615
		691.8	0.553
$K_2(SO_4WO_4)_{1/2}$		$LiK(SO_4WO_4)_{1/2}$	
992.0	1.481	973.5	1.509
979.8	1.449	956.8	1.464
963.2	1.417	934.0	1.405
945.5	1.381	913.5	1.353
928.8	1.339	879.2	1.259
		861.2	1.211
		848.0	1.176
		827.0	1.117
		810.0	1.061

Table 1. The specific electrical conductivity of the investigated salts.

Salt	a	$-b$	s	Range °C
K_2WO_4	0.22379	89.0	0.4	933—1036
$LiKWO_4$	0.21816	88.6	0.2	691— 918
$K_2(SO_4WO_4)_{1/2}$	0.24420	98.3	0.3	928— 992
$LiK(SO_4WO_4)_{1/2}$	0.23015	105.8	0.2	810— 974

Table 2. The molar electrical conductivity described by the relation $\Lambda = a\,t + b$, where t is the temperature in °C. s is the standard deviation.

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In Table 3 we have tabulated Λ at 900 °C and in Table 4 the ARRHENIUS activation energies (Q) obtained from

$$\Lambda = \Lambda_0 \exp(-Q/RT).$$

The standard deviation of Q is generally a few hundred cal/mole.

Anion / Cation	SO_4^{2-}	$(SO_4WO_4)_{1/2}^{2-}$	WO_4^{2-}
Li^+	121.1	89.7	69.6
$(LiK)_{1/2}^+$	61.3	50.7	44.3
K^+	67.3	60.7	55.0

Table 3. The equivalent conductivities of the investigated salts at 900 °C.

Anion / Cation	SO_4^{2-}	$(SO_4WO_4)_{1/2}^{2-}$	WO_4^{2-}
Li^+	2590	5180	5460
$(LiK)_{1/2}^+$	6420	6280	7530
K^+	4910	5440	5600

Table 4. The ARRHENIUS activation energies of the investigated salts.

Some regularities in Λ and Q can be observed.

a) If we have the same cation [Me = Li, K, $(LiK)_{1/2}$]

$$\Lambda(Me_2SO_4) > \Lambda(Me_2(SO_4WO_4)_{1/2}) > \Lambda(Me_2WO_4)$$

and $\Lambda(Me_2(SO_4WO_4)_{1/2})$ is not far from the mean value of the conductivities of the pure salts.

b) Λ(LiKX) [X = SO_4, WO_4, $(SO_4WO_4)_{1/2}$] is much smaller than both $\Lambda(Li_2X)$ and Λ(LiKX).

c) $Q(Me_2SO_4) < Q(Me_2(SO_4WO_4)_{1/2}) < Q(Me_2WO_4)$ except for LiKX, where

$$Q(LiK(SO_4WO_4)_{1/2}) \approx Q(LiKSO_4).$$

d) Q(LiKX) is much greater than $Q(Li_2X)$ and $Q(K_2X)$. For instance for the mixture of Li_2SO_4 and K_2WO_4, where $Q(Li_2WO_4) \approx Q(K_2WO_4)$, the activation energy is almost 40% higher than for the pure salts.

In the mixtures there is thus an increase in Q and a decrease in Λ compared with the pure salts if we have the same anion but different cations. This agrees with observations made for nitrate mixtures by others [8, 9]. On the other hand the conductivities and activation energies are almost ideal if we mix two salts with a common cation.

The difference in radius between the potassium ion and the lithium ion is the same as the difference between the tungstate ion and the sulphate ion (0.7 Å). The TOBOLSKY parameter [10] is thus approximately the same for LiKX and $Me_2(SO_4WO_4)_{1/2}$, but the deviations from ideality of the conductivities are very different. A possible explanation to this is that the transport mechanism mainly is determined by the cations in this system.

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Differential Thermal Analysis of Lithium Sulphate with Small Quantities of Sodium, Rubidium and Cesium Sulphate

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Previously obtained results for the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4 show a second order transition below the solidus curve, probably due to the rotation properties of the sulphate ions. To obtain more information about the high temperature behaviour, the systems $(Li,Na)_2SO_4$, $(Li,Rb)_2SO_4$ and $(Li,Cs)_2SO_4$ have been studied. From differential thermal analysis we have constructed the phase diagrams for Li_2SO_4 with small quantities of Na_2SO_4, Rb_2SO_4, and Cs_2SO_4.

Mechanical properties and electrical conductivity of the system $(Li,K)_2SO_4$ with small quantities of K_2SO_4 have recently been studied in this laboratory [1]. At a certain temperature below the solidus curve, a notable change in the temperature dependence of the apparent viscosity takes place, and a similar behaviour of the electrical conductivity is also observed. Our interpretation was that the sulphate lattice is affected by the presence of small amounts of foreign cations, and that this effect should depend on the size of the added ion. Considering data from X-ray measurements [2, 3] this effect would vanish if the foreign cation is small enough, but would appear for larger cations. A differential thermal analysis of the system $(Li,K)_2SO_4$ shows a change in the slope of the thermal curve at the considered temperature [1]. Similar systems could then be studied with this method.

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