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Electrical Conductivity of Molten NaCl–KCl–SrCl$_2$ Mixtures

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The specific electrical conductivity of molten NaCl–KCl–SrCl$_2$ mixtures was investigated in the temperature range 923–1123 K and in the concentration range of strontium chloride up to X_{SrCl_2} = 0.3. We found that the addition of strontium chloride to the liquid NaCl–KCl salt mixture decreases conductivity and that the conductivity increases with increasing temperature. Moreover, keeping the SrCl$_2$ content in the solution constant, one can decrease conductivity by adding KCl into the mixture. Our results suggest that the best conditions for electrolytic strontium production are achieved by locating the composition of the electrolyte close to the limiting NaCl–SrCl$_2$ binary system.

Introduction

Polish sulfur deposits are accompanied with strontium sulfate inclusions. Consequently, it is interesting to consider conditions for extracting pure strontium metal, which in turn may find numerous applications in modern technology. Generally, there are two possible ways to achieve this aim: aluminothermic reduction of strontium oxide and electrolysis from molten salts.

The system of alkali chlorides containing SrCl$_2$ is seen as a potential electrolyte for the latter process. Control of the electrolysis demands a deep knowledge of a number of physicochemical properties of the electrolyte. The specific electrical conductivity is that one which directly influences the efficiency of the process. Thus, any design of the electrolytic process requires reliable information on the conductivity of the electrolyte as well as knowledge of the phase diagram of the system employed as the electrolyte.

Experimental Determination of the Liquidus Surface of the SrCl$_2$-Deficient Part of the NaCl–KCl–SrCl$_2$ System

On one hand, the electrolyte chosen for a technological process should exhibit a relatively low melting temperature. On the other hand, the chosen range of temperatures and compositions should not retard the efficiency of the process. The ternary NaCl–KCl–SrCl$_2$ phase diagram was given by Voskresenskaya et al. (*1*). It indicates that starting from an equimolar NaCl–KCl salt mixture, the temperature of the liquidus decreases from about 923 to 823 K as the strontium chloride content increases to about 0.5 mole fraction of SrCl$_2$. Thus, if the salt mixture mentioned above is to be used for the electrolyte, at least this part of the phase diagram as well as the corresponding electrical conductivities should be known. However, a recently published phase diagram (*2*) indicates the existance of a third eutectic in the considered concentration range that differs from that one given in ref 1.

We started our study by reexamining this part of the NaCl–KCl–SrCl$_2$ phase diagram. Investigations of the liquidus temperature were carried out using the differential thermal analysis (DTA) apparatus of Paulik, Erdey and Paulik. Charges of salt mixture with masses of 400 mg were prepared by mixing dry, powdered, reagent grade chemicals. Next, the samples were placed in the DTA apparatus in alumina crucibles under a stream of dry argon. The temperature was increased at a rate of either 5 or 10 °C/min. α-Al$_2$O$_3$ was used as a reference substance. The compositions of the salt mixtures and corresponding liquidus temperatures are given in Table I. From these results, isothermal liquidus curves were constructed and are shown together with those previously reported (*1*) in Figure 1. Liquidus temperatures of respective binary phase diagrams were accepted after ref 1. It is clear that, along with X_{NaCl}/X_{KCl} = 1, the ternary system liquidus temperature decreases steadily with increasing SrCl$_2$ content up to about X_{SrCl_2} = 0.35. This observation is compatible with results reported in refs 1 and 2.

Table I. Experimental Liquidus Temperature from DTA Measurements

no.	X_{SrCl_2}	X_{KCl}	X_{NaCl}	T liquidus av value (±5 K), K
1	0.10	0.50	0.40	898
2	0.10	0.45	0.45	898
3	0.10	0.40	0.50	893
4	0.15	0.45	0.40	878
5	0.15	0.425	0.425	878
6	0.15	0.40	0.45	890
7	0.20	0.50	0.30	873
8	0.20	0.42	0.38	873
9	0.20	0.30	0.50	903
10	0.30	0.45	0.25	903
11	0.30	0.35	0.35	853
12	0.30	0.25	0.45	878

Experimental Determination of the Specific Electrical Conductivity in Molten NaCl–KCl–SrCl$_2$ Mixtures

The scheme of our conductometric cell is shown in Figure 2. An experimental method and procedure were described previously (*3*). The container of the cell was made of graphite with the alumina shield inside. Current leads of both electrodes were made of molybdenum wires (4-mm o.d.), which were kept inside alumina shields. Powdered NaCl–KCl–SrCl$_2$ mixtures kept inside the container were prepared from dried reagent grade chemicals. Melting and conductivity measurements were carried out under dried argon. The position of the movable electrode was adjusted by using a micrometer. The measurements were carried out at a frequency of 18 kHz with currents of 5–20 mA. Resistivity of the electrolyte was determined from the voltage drop across the layer of the electrolyte. Current density was measured from the voltage drop across a standard resistor with a resistance of 1 Ω. The temperature in the melt was measured with a Pt-PtRh10 thermocouple with the accuracy of ±2 K. The equilibration of the cell resistance was measured by means of a Wheatstone bridge. The specific conductivity, κ (Ω^{-1} cm^{-1}), was calculated from the relation

$$\kappa = \frac{1}{(R/l)S} \tag{1}$$

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Table II. Specific Electrical Conductivity of the NaCl-KCl-$SrCl_2$ Liquid Mixtures

				κ, Ω^{-1} cm^{-1}				
no.	X_{NaCl}	X_{KCl}	X_{SrCl_2}	923 K	973 K	1023 K	1073 K	1123 K
1	0.5	0.5		2.21 (±0.014)	2.35 (±0.010)	2.50 (±0.013)	2.65 (±0.012)	2.80 (±0.015)
2	0.7		0.3	2.47 (±0.01)	2.61 (±0.012)	2.79 (±0.011)	3.05 (±0.010)	3.18 (±0.010)
3	0.4	0.5	0.1	2.01 (±0.012)	2.14 (±0.010)	2.23 (±0.012)	2.38 (±0.012)	2.49 (±0.011)
4	0.45	0.45	0.1	1.98 (±0.011)	2.21 (±0.010)	2.355 (±0.011)	2.50 (±0.010)	2.65 (±0.014)
5	0.5	0.4	0.1	2.08 (±0.01)	2.205 (±0.01)	2.32 (±0.014)	2.43 (±0.016)	2.505 (±0.016)
6	0.38	0.42	0.15	1.85 (±0.01)	1.94 (±0.006)	2.01 (±0.01)	2.11 (±0.012)	2.17 (±0.012)
7	0.425	0.425	0.15	1.975 (±0.01)	2.13 (±0.01)	2.275 (±0.012)	2.42 (±0.017)	2.57 (±0.012)
8	0.4	0.45	0.15	1.91 (±0.01)	2.05 (±0.011)	2.19 (±0.01)	2.33 (±0.012)	2.47 (±0.01)
9	0.3	0.5	0.2	1.84 (±0.01)	1.91 (±0.015)	1.975 (±0.01)	2.04 (±0.015)	2.10 (±0.01)
10	0.38	0.42	0.2	1.85 (±0.01)	1.94 (±0.01)	2.01 (±0.01)	2.11 (±0.012)	2.17 (±0.012)
11	0.5	0.3	0.2	1.935 (±0.01)	2.01 (±0.012)	2.09 (±0.02)	2.17 (±0.018)	2.21 (±0.016)
12	0.25	0.45	0.3	1.61 (±0.012)	1.69 (±0.01)	1.77 (±0.02)	1.86 (±0.015)	1.94 (±0.02)
13	0.35	0.35	0.3	1.76 (±0.015)	1.82 (±0.01)	1.88 (±0.016)	1.925 (±0.015)	2.01 (±0.02)
14	0.45	0.25	0.3	1.805 (±0.01)	1.87 (±0.01)	1.935 (±0.02)	1.995 (±0.01)	2.05 (±0.012)

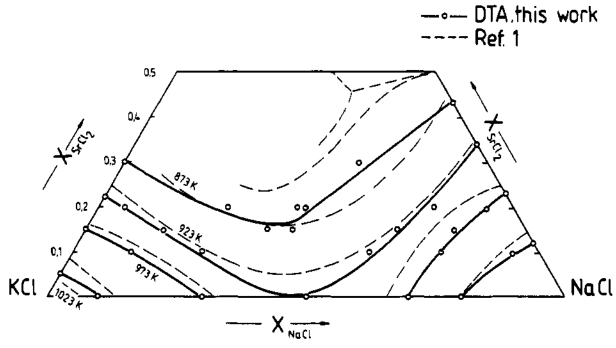

Figure 1. Part of the NaCl-KCl-$SrCl_2$ phase diagram.

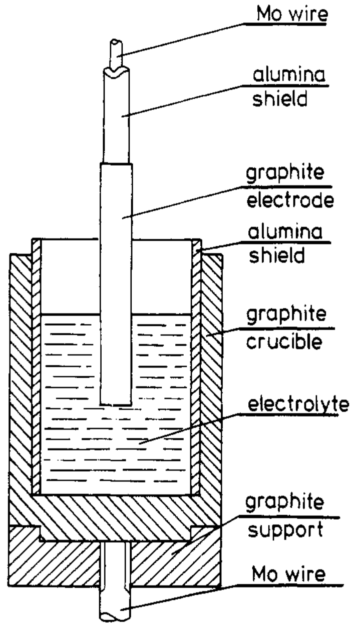

Figure 2. Scheme of the conductometric cell.

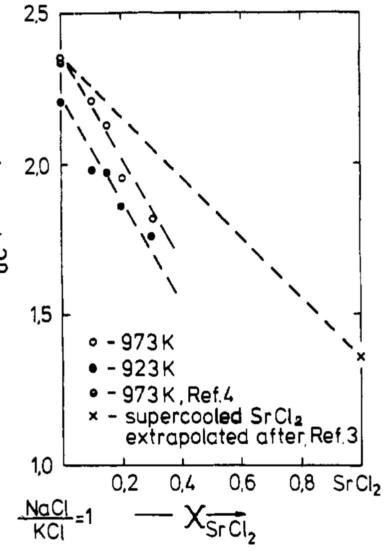

Figure 3. Specific conductivity κ as a function of X_{SrCl_2} for the ratio $X_{NaCl}/X_{KCl} = 1$.

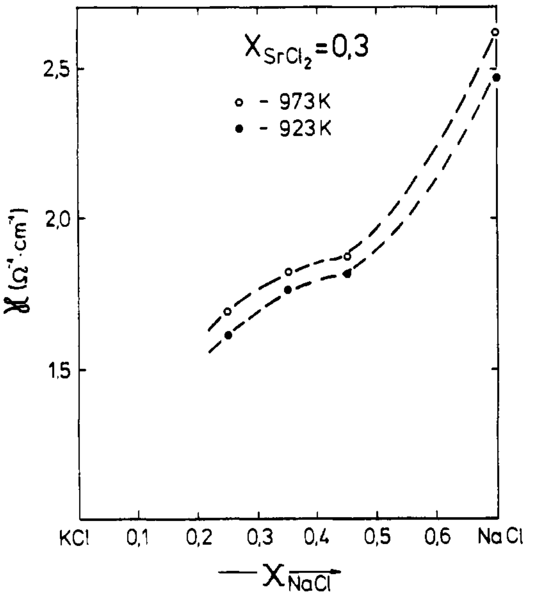

Figure 4. Specific conductivity κ as a function of X_{NaCl} for X_{SrCl_2} = 0.3.

where (R/l) is the resistivity charge across electrolyte layer of the height l and S is the active area of the electrodes in cm^2, which is equal to the cell constant.

The cell was calibrated by using pure sodium chloride, and the cell constant S was determined experimentally as $S = 1/\kappa_{NaCl}(R/l)$ at fixed $T = 1113$ K. It was found that S is equal to 22.175 ± 0.514 cm^2. Results obtained at increasing and decreasing temperatures for fixed compositions of the salt mixture are presented in Table II. Two different effects concerning the conductivity change with the salt composition are observed:

(1) For a fixed NaCl/KCl ratio, the addition of $SrCl_2$ decreases the conductivity. This effect is demonstrated in Figure 3 for the X_{NaCl}/X_{KCl} ratio equal to one. Conductivity falls with increasing $SrCl_2$ content but increases with temperature. The hypothetical value of specific conductivity for pure, liquid, supercooled $SrCl_2$ shown in Figure 3 at 973 K was calculated by extrapolation of

an equation given by Janz (*4*).

(2) For fixed $SrCl_2$ content in the melt, the addition of NaCl increases the conductivity. This effect is shown in Figure 4 for $X_{SrCl_2} = 0.3$. For increasing KCl content and fixed $SrCl_2$ composition, conductivity decreases rapidly at constant temperature. Again, higher temperature yields higher specific conductivity.

Discussion

The reliability of conductivity measurements reported in this study was checked by comparing κ values obtained at 973 K for the NaCl–KCl system with results by Matiašovsky et al. (*5*). Their value obtained for the equimolar NaCl–KCl mixture, 2.338 Ω^{-1} cm^{-1}, is in excellent agreement with the value obtained in the present study, 2.35 ± 0.01 Ω^{-1} cm^{-1}. Thus, one can assume that dependences observed in the ternary NaCl–KCl–$SrCl_2$ system can be trusted.

Keeping in mind that one is looking for a composition of a potential electrolyte, it should be assumed that $SrCl_2$ content in the salt mixture cannot be too high. The solubility of strontium in pure strontium chloride is high. At elevated temperatures it varies from about 6 mol % at monotectic temperature 1112 K (*6*) to about 25 mol % at the temperature 1273 K (*7*). There is a real danger that due to this phenomenon high $SrCl_2$ content in the electrolyte can affect efficiency of the process. At the same time, an increase of the $SrCl_2$ content decreases the conductivity. Thus, it is suggested for the above reasons that $X_{SrCl_2} = 0.3$ should not be exceeded.

The choice of the KCl/NaCl ratio at fixed X_{SrCl_2} depends on the choice between the temperature of the process and the conductivity of the electrolyte. The KCl–$SrCl_2$ phase diagram (*1*) indicates the existence of two double compounds, $2KCl{\cdot}SrCl_2$ and $KCl{\cdot}2SrCl_2$. Their presence must correspond to the appearance of complex ions in the liquid, probably of the $SrCl_4^{-2}$ type. The resulting mobility of Sr^{2+} ions must fall, and the transference number, $t_{Sr^{2+}}$, must be very small. This kind of phenomenon was observed in the KCl–$MgCl_2$ solution (*8*). Thus, the rapid decrease of conductivity shown in Figure 4 for KCl-rich compositions may follow directly from complex ion formation. For this reason, the composition of the potential electrolyte should be located close to the limiting binary NaCl–$SrCl_2$ system, where the conductivity of the liquid electrolyte is higher. However, the temperature of the process may require the shift of the electrolyte composition toward the KCl-rich side, where the liquidus temperature is lower. This optimum must be found through further experimentation.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; $SrCl_2$, 10476-85-4.

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Micellar Behavior of Praseodymium Valerate Dissolved in Binary Methanol and Benzene Mixtures

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Conductance results showed that praseodymium valerate behaves as a weak electrolyte in dilute solutions below the critical micelle concentration (cmc) and the cmc increases with increasing temperature. The various thermodynamic parameters were also evaluated for both dissociation and micellization processes. The viscosity data were interpreted in light of well-known equations. The ultrasonic velocities in the soap solutions were measured, and the results were used to evaluate thermodynamic and acoustic parameters. The results of cmc were found in excellent agreement with those obtained from other properties.

Introduction

Studies on the utilization of metallic soaps in various industries are still being carried out as the problem is of immense importance from pharmaceutical and technical points of view. The practical utility of these metal soaps has attracted the attention of several workers, as their physicochemical characteristics and structure largely depend on the conditions and methods of preparation. The survey of literature reveals that very few references are available on rare-earth metal soaps (*1–10*).

The micelle formation in a solvent depends upon its solubility parameter and ability to solvate the surfactant. The lower praseodymium soaps possess higher solubility in mixed solvents (methanol–benzene mixtures) rather than in pure solvents (methanol or benzene) and have been chosen to study the behavior of these soaps in such solvents. In this paper we report experimental conductivity, viscosity, and ultrasonic data for praseodymium valerate dissolved in binary mixtures containing benzene and methanol. Results of these measurements are used to calculate thermodynamic, interactional, and acoustical parameters.

Experimental Section

All the chemicals used were of BDH/AR grade. Praseodymium valerate was prepared by the direct methathesis of the corresponding potassium soap with the required amount of aqueous solution of praseodymium nitrate at 50–60 °C under

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