

# The Electric Conductivities and Densities of Molten $\text{SnCl}_2$ - $\text{ZnCl}_2$ Binary Mixtures

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The specific electric conductivities and densities of molten  $\text{ZnCl}_2$ - $\text{SnCl}_2$  binary mixtures were measured as a function of composition in the temperature range 260–530 °C. The electric conductivities show small, mainly negative, deviations from additivity. The densities show positive deviations from additivity, especially in the  $\text{SnCl}_2$ -rich composition range. The structural properties of the melts causing such a behaviour are discussed.

## Introduction

The electric conductivities<sup>1–4</sup>, densities<sup>3, 5, 6</sup> and viscosities<sup>3, 7</sup> of the  $\text{ZnCl}_2$  melt have been intensely investigated. This melt has high temperature coefficients of the electric conductivity and viscosity in the low temperature region, and easily forms a glassy state on solidifying<sup>8</sup>. These properties have been explained by the existence in the melt of large clusters of the formulae  $[(\text{ZnCl}_2)_x\text{Cl}_p]^{p-}$  and  $[(\text{ZnCl}_2)_x\text{Zn}_q]^{2q+}$  arising from an incomplete destruction of the layers of the  $\text{ZnCl}_2$  crystal lattice<sup>3, 7</sup>. As the temperature increases the clusters decrease and the melt acquires more and more the properties of ionic melts. The electric conductivities<sup>9, 10</sup>, densities<sup>10–12</sup> and viscosities<sup>13</sup> of the molten systems  $\text{ZnCl}_2$ -alkali halogenide have also been investigated.

The electric conductivities of these systems as a function of mole composition exhibit both positive and negative deviations from additivity.

The partial molar volumes of  $\text{ZnCl}_2$  in these systems decrease with increasing mole fraction of alkali halogenide<sup>11</sup>. In correlation with the phase diagram<sup>10</sup> such deviations are explained by formation of complex compounds in the melt or by destruction of the associated structure of the  $\text{ZnCl}_2$  melt on addition of purely ionic melts<sup>9–11</sup>.

The electric conductivity<sup>1, 4</sup> and viscosity<sup>14</sup> of the  $\text{SnCl}_2$  melt in the vicinity of the melting point have temperature coefficients higher than those of purely ionic melts of alkali halogenides but considerably lower than those of molten zinc halogenide. The phase diagram of the  $\text{SnCl}_2$ - $\text{ZnCl}_2$  system<sup>15</sup> is simple, with one eutectic, which is indicative of weak interactions between ions and molecules in the melt of the binary system.

## Experimental

Merck  $\text{ZnCl}_2$  and  $\text{SnCl}_2$  were dried at 200 °C in an atmosphere of argon. After drying, the salts were fused and gaseous dry HCl was passed through the melts for several hours in order to purify them from the products of hydrolysis. The melts were then filtered through filters made of sintered glass.

Mixtures of the molten salts were obtained by introducing with a pipette different amounts of each component into a measuring cuvette. The Pyrex cuvette, 2 cm in diameter, was filled with the melt to a height of 3 cm and placed in a metal block, 3 cm in diameter, in the central part of a furnace 6 cm wide and 50 cm high. The role of the metal block was to minimize the thermal gradient over the height of the cuvette.

The temperature was measured with an accuracy to within  $\pm 1$  °C with a calibrated chromel-alumel thermocouple, which, protected by a quartz tube, was immersed directly in the melt.

The electric conductivities were measured with the apparatus described previously<sup>16</sup>. Use was made of an immersion cell with platinum electrodes, whose constant was determined by measurement of the resistance of the  $\text{ZnCl}_2$  melt at different temperatures, on the basis of tabulated data on its conductivity<sup>17</sup>. Measurements of electric conductivity were carried out simultaneously with those of density.

The density was measured by the method of hydrostatic lift, using a body of Pyrex glass with submerged iron suspended by a thin platinum wire 0.02 cm in diameter. The volume of this body was determined as a function of temperature by measurement of the lift in the  $\text{ZnCl}_2$  melt, on the basis of tabulated data on densities of the  $\text{ZnCl}_2$  melt<sup>17</sup>. Measurements were not made at temperatures above 530 °C because of the relatively high volatility of molten  $\text{SnCl}_2$  and its chemical instability in the presence of  $\text{O}_2$ .



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The mole composition of the mixtures was determined polarographically by taking with a pipette a sample mixture before and after each measurement of the density and conductivity as a function of temperature respectively. Experiments in which the mole compositions in the beginning differed from those at the end were left out of account.

### Results

Figure 1 shows experimentally determined electric conductivities of molten  $\text{ZnCl}_2$ – $\text{SnCl}_2$  mixtures as a function of mole composition at different temperatures. From the slope of the  $\ln \kappa$ –versus  $-1/T$  plot the activation energies for specific conduction were determined as a function of mole composition at a temperature of 450 °C. The results are presented in Figure 2.

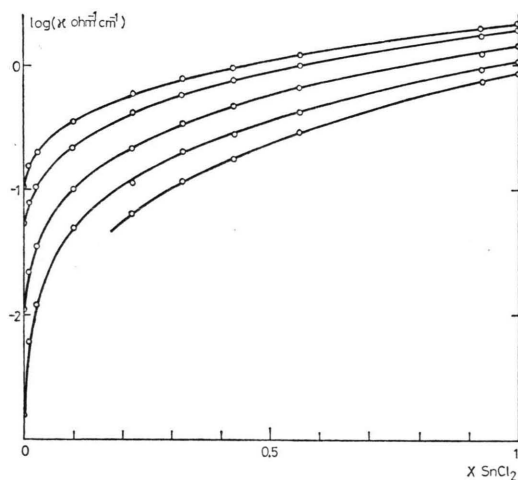


Fig. 1. The logarithm of specific electric conductivity of the molten  $\text{SnCl}_2$ – $\text{ZnCl}_2$  system as a function of mole fraction of  $\text{SnCl}_2$  at the following temperatures (from the top downward): 509, 457, 357, 300, 265 °C.

The deviations of electric conductivity from additivity are not considerable. They are negative at lower temperatures and positive at higher ones in the  $\text{ZnCl}_2$ -rich composition range (Figure 3).

The densities of the binary system as a function of mole composition at different temperatures are presented in Figure 4. Deviations from additivity are positive at all temperatures and compositions, and are more pronounced in the  $\text{SnCl}_2$ -rich composition range. Figures 5 and 6 present partial molar volumes of molten  $\text{SnCl}_2$  and  $\text{ZnCl}_2$  as determined by the method of intercepts on the molar volume-versus-mole fraction diagram. The partial

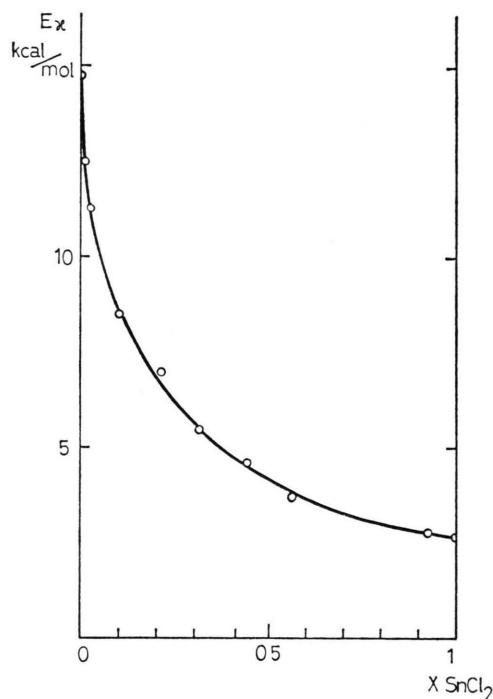


Fig. 2. The activation energy for specific electric conduction of the molten  $\text{SnCl}_2$ – $\text{ZnCl}_2$  system as a function of mole fraction of  $\text{SnCl}_2$  at a temperature of 450 °C.

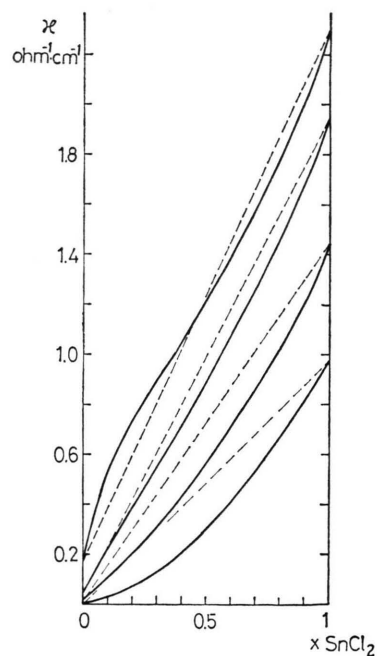


Fig. 3. Specific conductivities of the molten  $\text{SnCl}_2$ – $\text{ZnCl}_2$  system as a function of mole fraction of  $\text{SnCl}_2$  at the following temperatures (from the top downward): 509, 457, 360, 282 °C.

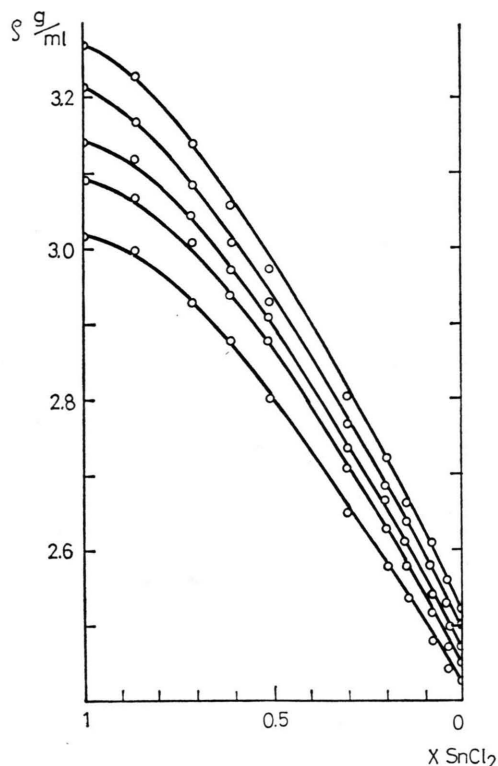


Fig. 4. Densities of the molten  $\text{SnCl}_2$ - $\text{ZnCl}_2$  system as a function of mole fraction of  $\text{SnCl}_2$  at the following temperatures (from the top downward): 317, 376, 427, 467, 527 °C.

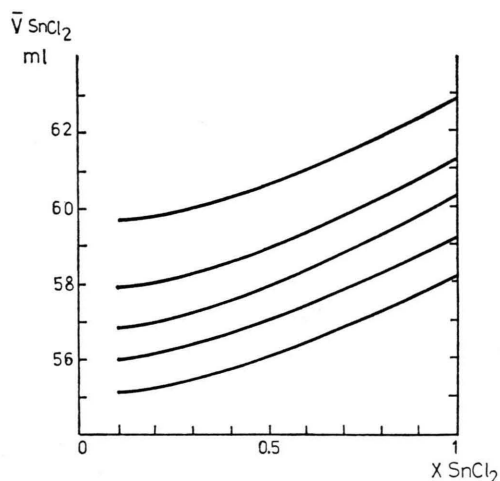


Fig. 5. Partial molar volumes of molten  $\text{SnCl}_2$  as a function of its mole fraction in the molten  $\text{SnCl}_2$ - $\text{ZnCl}_2$  system at the following temperature (from the top downward): 527, 467, 427, 367, 317 °C.

molar volume of molten  $\text{SnCl}_2$  increases slowly as its mole fraction increases. The partial molar volume of molten  $\text{ZnCl}_2$  rapidly increases at lower mole

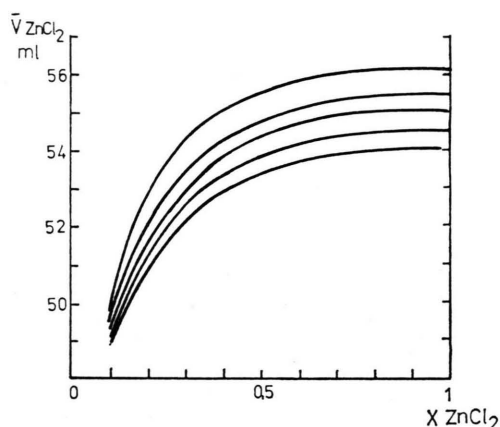


Fig. 6. Partial molar volumes of  $\text{ZnCl}_2$  as a function of its mole fraction in the molten  $\text{SnCl}_2$ - $\text{ZnCl}_2$  system at the following temperatures (from the top downward): 527, 467, 427, 367, 317 °C.

fractions, while at higher ones it increases slowly with increasing mole fraction.

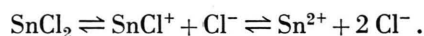
### Discussion

Positive and negative deviations from additivity of molar volumes of molten binary mixtures are explained by complexing and increase of ionic character of the melt with changing mole composition<sup>9, 11, 18-20</sup>. Small deviations of molar volumes are accompanied by relatively large deviations of electric conductivity from additivity. In the  $\text{ZnCl}_2$ - $\text{SnCl}_2$  system, however, considerable deviations of molar volumes from additivity are accompanied by unusually small deviations of electric conductivity from additivity (Figure 3).

We propose the following explanation of these phenomena:

The  $\text{ZnCl}_2$  melt has a large number of intermolecular holes due to a statistical distribution of the clusters mentioned in the introductory part of the present paper, which are carriers of the electrical and viscous properties of the melt.

The  $\text{SnCl}_2$  melt, as indicated by the order of magnitude and temperature dependence of electric conductivity and viscosity, has a structure determined by the equilibrium:



The equilibrium is rapidly shifted to the right as the temperature is increased. Relatively small structural units make this melt compact, i. e. poor in intermolecular holes.

Addition of a small amount of molten  $\text{ZnCl}_2$  to the  $\text{SnCl}_2$  melt gives rise to a minimum increase in the total volume of the system, since flat  $\text{ZnCl}_2$  clusters are arranged closely in the  $\text{SnCl}_2$  melt, as shown schematically in Figure 7. Because of the weak interionic interactions this process does not lead to any considerable deviations of electric conductivity from additivity. The effect of complexing or increase of electrolytic dissociation should not be disregarded, but we consider spatial effects to be

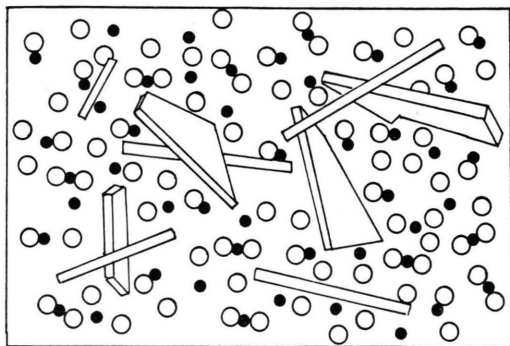


Fig. 7. A model of the molten  $\text{SnCl}_2$ — $\text{ZnCl}_2$  binary mixture at higher mole fractions of  $\text{SnCl}_2$ :  $\square$  parts of the chlorine-layer crystal lattice of  $\text{ZnCl}_2$ ;  $\bullet$  the  $\text{Sn}^{2+}$  ions;  $\circ$  the  $\text{Cl}^-$  ions.

predominant in this system. This model is also in accordance with the results of Bloom and Weeks<sup>11</sup>, who have found that the partial molar volume of  $\text{ZnCl}_2$  increases as its mole fraction increases in mixtures with alkali chloride melts. In the systems  $\text{ZnCl}_2$ — $\text{NaCl}$  and  $\text{ZnCl}_2$ — $\text{CsCl}$ <sup>9</sup>, as well as in our system (Fig. 2), the activation energies for electric conduction already at a mole fraction of 0.3 of the components  $\text{NaCl}$ ,  $\text{CsCl}$  and  $\text{SnCl}_2$  are close to those of either pure component. That means that already at mole fractions above 0.3 practically all the current is carried by the components which are stronger electrolytes, while  $\text{ZnCl}_2$  serves as their diluter. The sharp decrease in the activation energy for electric conduction is not caused by an increase of ionic character of the  $\text{ZnCl}_2$  melt and by decomposition of its clusters, since this effect would be accompanied by a positive deviation of electric conductivity from additivity. In accordance with this point of view, we attribute negative deviations of electric conductivity from additivity in this system to the high viscosity of the  $\text{ZnCl}_2$  melt rather than to other possible effects which require stronger interactions between components (e. g. formation of less electrolytically dissociated complexes).

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