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Rapid Communication

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Electrical Conductivity of Molten $CdCl_2$ at Temperatures as High as 1474 K

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Abstract: The electrical conductivity of molten $CdCl_2$ was measured across a wide temperature range ($\Delta T = 628$ K), from 846 K to as high as 1474 K, i.e. 241° above the normal boiling point of the salt. In previous studies, a maximum temperature of 1201 K was reached, this being 273° lower than in the present work. The activation energy of electrical conductivity was calculated.

Keywords: Cadmium Dichloride; Electrical Conductivity; Molten Salts.

1 Introduction

Molten salts have a potential capacity as non-aqueous electrolytes; therefore, reliable information on their electrical conductivity is required. However, due to significant experimental difficulties experienced when the vapour pressure of salts reaches several atmospheres at the high temperatures, most of the existing data were obtained across a narrow temperature range close to the melting points of the salts [1]. There are only a few studies in which measurements have been performed across a wide temperature range and under essentially high vapour pressure, for example [2–6]. In particular, until now the electrical conductivity of molten $CdCl_2$ has been unknown at temperatures higher than its normal boiling point of 1233 K [7].

The purpose of this work is to measure the electrical conductivity of molten $CdCl_2$ at high temperatures as we did earlier for $ZnCl_2$ [8] and $SnCl_2$ [9] melts.

2 Experimental

An analytical grade $CdCl_2{\cdot}2.5H_2O$ (99.7 %) salt was carefully dehydrated through long-term (about 9 h) gradual heating up to 720 K under reduced pressure (~1 Pa) and then additionally purified by distillation under dynamic vacuum of ~1 Pa at 770–890 K. The final purity of the product ($CdCl_2$) exceeded 0.9998 (mass fraction) [10].

The electrical conductivity measurements of molten $CdCl_2$ were carried out in quartz capillary-type cells of two different designs. In the temperature range of 846–1097 K, a U-shaped cell with platinum electrodes was used (first type) [10, 11]. At higher temperatures (940–1474 K), when the vapour pressure reached 1.5 MPa [7], a hermetically sealed cell with W-electrodes of a special type was utilised [4, 12]. It should be emphasised that we did not apply an external pressure since the high pressure in the cells was the self-generated pressure of the saturated vapour of the salt under investigation.

The cells were charged in a dry glove box, sealed, and then heated in an electric furnace equipped with a metallic block. The melt temperature was recorded with an accuracy of ±1 K using a Pt–PtRh (10 % Rh) thermocouple. The melt resistance was measured by an AC-bridge at an input frequency of 10 kHz.

The cell of the first type was calibrated against a standard 1-molal KCl solution [13], while the second type of cell was calibrated against the electrical conductivity of the molten $CdCl_2$, obtained in the cell of the first type [10]. A cell constant ranged from 72.9 cm^{-1} to 91.1 cm^{-1}. The design of the cells and measuring procedures are described in more detail elsewhere [10–12].

3 Results and Discussion

The results of the molten $CdCl_2$ electrical conductivity measurements are shown in Figure 1. The data obtained with the use of “low-temperature” and “high-temperature” cells, as well as at the heating and cooling of the melts, are in good agreement with each other. Therefore, all results were approximated by a single equation:

$$\kappa = -1.8255 + 5.9723\times10^{-3}\cdot T - 1.8808\times10^{-6}\cdot T^2,\ \text{S/cm};\quad T,\ \text{K}\quad \Delta T = 846\text{–}1474\ \text{K}. \tag{1}$$

The determination coefficient $R^2 > 0.999$; the standard deviation $\kappa = 0.001$. The overall error of determining κ [10, 12] does not exceed 2 % across the entire temperature range.

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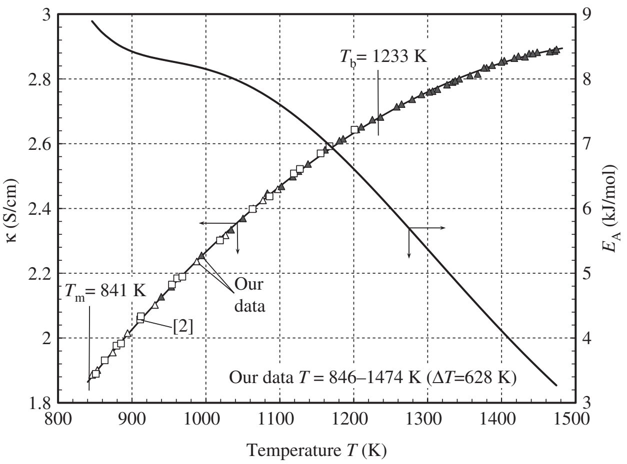

Figure 1: Specific conductivity (κ) polytherms of molten $CdCl_2$ and its activation energy (E_A). T_m and T_b are melting and boiling temperatures, respectively. Δ – our data, obtained in the capillary "low-temperature" cell. ▲ – our data, obtained in the "high-temperature" cell.

According to the structural studies [14, 15], a tetrahedral coordination $CdCl_4^{2-}$ predominates in molten $CdCl_2$. The covalent forces between cadmium and halogen are rather weak; an ionic character prevails in the melt. Our electrical conductivity measurements strongly support this view. When the molten cadmium chloride is heated from 846 to 1474 K ($\Delta T = 628$ K), κ increases from 1.886 to 2.891 S/cm. The increase in electrical conductivity apparently occurs mainly due to an increase in ion mobility. By comparison, in previously investigated strongly associated molten $ZnCl_2$, the electrical conductivity rose by several orders of magnitude as a result of the disintegration of its network structure as the temperature increases [8].

The review of works on molten $CdCl_2$ electrical conductivity is given in the handbook [1]. Our results are in good agreement with the most reliable of them. For example, the difference between our results and the data for the highest temperature ($T_{max} = 1201$ K) studies existing in the literature [2] does not exceed 0.3 %. There are only three works whose results differ from our results by more than ±2 %. The maximum discrepancy between our data and [16] is $\delta = +4.3\,\%$, with [17] $\delta = +2.4\,\%$, and [18] −4.1 %. The difference may be attributed to imprecise cell calibration.

It is hypothesised that the electrical conductivity polytherms of all molten salts pass through their maxima in the temperature range from the melting point to the critical point [3]. For example, the electrical conductivity of molten $BiCl_3$ passes through a maximum at 425 °C, $SnCl_2$ at 875 °C, and CdI_2 at 1085 °C [3, 9]. Upon heating, the increase in the conductivity of molten $CdCl_2$ gradually slows down (Fig. 1) and the conductivity activation energy decreases from ~8.9 to ~3.3 kJ/mol in the range of 846–1474 K. However, even at 1474 K, the κ maximum has still not been reached: measurements were no longer possible at the point when the pressure in the cell exceeded 1.5 MPa [7]. According to [3] maximum of conductivity polytherm is reached at about 1570 K.

Solutions of metal in molten salts have been the subject of many studies. In particular, Grantham [2] measured the conductivity of $CdCl_2$–10.09 at % Cd solutions up to 1479 K and the electrical conductivity of pure $CdCl_2$ only to 1201 K due to experimental difficulties. Our new experimental data together with the data [2] allow the effect of dissolved metal on the melt conductivity to be evaluated up to very high temperatures as follows: –3.1 % (873 K), –1.1 % (973 K), ~0 % (1083 K), +0.7 % (1173 K), +1.7 % (1273 K), +3.7 % (1373 K), and +9.1 % (1473 K). It is known [2, 14] that the dissolution of metallic Cd in molten $CdCl_2$ melts at temperatures close to the melting temperature of the salt occurs with the formation of a stable diatomic subvalent Cd_2^{2+} species surrounded by four Cl^- anions as well as in $CdCl_4^{2-}$ groups. This leads to a slight decrease in the electrical conductivity. With increasing temperature, the negative deviations are replaced by positive ones. They reach +9.1 % at 1473 K, according to our data. The formation of simpler Cd^+ ions (non-dimers) and the appearance of electronic conductivity are conceivable reasons for the conductivity increasing at high temperatures when metallic cadmium is added.

To confirm the suggestions, additional direct structural studies of the high-temperature melts are required.

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