

**Letter to Editor**

**ON THE SURFACE TENSION OF METHAPHOSPHATE MELTS  
STUDIED BY THE RING METHOD**

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**Abstract**

*Surface tensions of the  $MPO_3$  ( $M = Rb, Cs$ ) melts were determined from high temperature experiments performed under Ar atmosphere, by means of the ring method using a Du Noüy tensiometer. The surface tension data were fitted by linear regression at the temperature range from 1123 up to 1373 K. A good correlation was observed between experimentally measured surface tension data and that known from the literature. It was suggested that coordination and ionic potential of cation determine character of the coulomb interaction weakening with the temperature increase for each of the  $MPO_3$  melts compared.*

*Keywords: Ring Du Noüy tensiometry; Molten salts; Thermal analysis*

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**1. Introduction**

The molten salt electrolysis is a technique allowing converting metal oxides directly into the corresponding parent metals (alloys) by way of electrochemical reduction in a molten salt electrolyte. Creation of data base on physicochemical properties of inorganic molten salts prospective to be implemented into electrolytic metallurgical processes is an actual task. Among the salts, phosphates are

of great interest as components of molten salt bathes used for electrowinning, electrorefining, and electroplating of refractory metals [1]. As surface tension effects on such melt parameters as adhesion, reactivity and wetting penetration, and these parameters determine a choice of container materials for industrial operations with the melt, so accurate data for the surface tension of molten phosphates are always desirable to meet operational demands. While a

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numerous melts properties are intensively examined up to the present time, there are relatively few papers on the surface tension of molten alkaline methaphosphates [2, 3]. Considering the limited availability of the surface tension data, the present work was undertaken to obtain maximal data set for the surface tensions of  $MPO_3$  ( $M = Rb$  and  $Cs$ ) melts.

## 2. Experimental Details

The homogeneous and transparent  $MPO_3$  ( $M = Rb$  and  $Cs$ ) methaphosphates were prepared by dehydration of  $RbH_2PO_4$  and  $CsH_2PO_4$  (all from Sigma-Aldrich, 99.99%+). The X-ray diffraction patterns of the methaphosphates recorded with a X-ray powder diffractometer (Philips PW 3020,  $CuK\alpha$ -radiation) show broad and diffused humps that indicate the amorphous nature of the synthesized samples. The atomic adsorption spectrophotometry analysis of the samples with Perkin-Elmer AAS Model 603 instrument was revealed the presence of  $Cs$  or  $Rb$  and  $P$  in equimolar ratio. According to differential thermal analysis data registered with a Q-1500 derivatograph, the methaphosphates melt at  $1079 \pm 7$  K ( $RbPO_3$ ) and  $997 \pm 5$  K ( $CsPO_3$ ) that agrees well with results of [4]. The samples obtained were regrinded and remelted at 1173 K in order to measure the melts properties. The measurements of the surface tensions were carried out under Ar atmosphere, using the ring method with a Du Noüy tensiometer at the temperature interval from 1123 K to 1373 K. The apparatus, measurements and calibration routine were reported previously in [2].

## 3. Results and Discussion

The surface tension ( $\gamma$ ) of the melts studied decreases with temperature,  $\gamma(T, K)$  dependence shows a linear behavior. The experimental  $\gamma$  values measured at  $1123 \leq T, K \leq 1373$  were treated by a least square regression method [4] as follows:

$$\gamma \text{ (mN} \cdot \text{m}^{-1}\text{)} = 178.3 \pm 1.2 - 0.047 \pm 0.002 T / K \text{ for RbPO}_3 \quad \dots(1)$$

$$\gamma \text{ (mN} \cdot \text{m}^{-1}\text{)} = 162.0 \pm 2.0 - 0.053 \pm 0.003 T / K \text{ for CsPO}_3 \quad \dots(2)$$

In Ref. [5] it was suggested that  $\gamma(RbPO_3) = 124 \text{ mN} \cdot \text{m}^{-1}$  at  $T_m = 1098$  K, consequently extrapolation of (1) on 1098 K leads to  $\gamma_{1098 \text{ K}} = 126.7 \text{ mN} \cdot \text{m}^{-1}$ , which is in a good agreement with [6]. Collected  $\gamma$  data for the  $CsPO_3$  melt are overstated relatively to ones of [6]; the latter can be expressed as

$$\gamma \text{ (mN} \cdot \text{m}^{-1}\text{)} = 153.0 \pm 4.0 - 0.049 \pm 0.022 T / K \text{ for } 1010 < T, K < 1314 \quad \dots(3)$$

using initial  $\gamma$  data set determined by the maximal bubble pressure method.

The linear trend of  $\gamma$  against temperature is typical for all methaphosphate melts [3], similar decreasing of the  $\gamma$  values was reported earlier for the  $KPO_3$  melt [2] and fitted as

$$\gamma / \text{(mN} \cdot \text{m}^{-1}\text{)} = 202.0 \pm 2.5 - 0.062 \pm 0.001 T / K \text{ for } 1073 < T, K < 1373 \quad \dots(4)$$

For all  $MPO_3$  melts studied the surface tension decreases in a sequence  $CsPO_3 < RbPO_3 < KPO_3$ , hence the negative values of the thermal coefficient ( $dy/dT$ ) are rather close and increase in the order  $Rb < Cs < K$ .

If compare with fused  $P_2O_5$ , which  $\gamma$  values are ranged from 50 to 60  $mN \cdot m^{-1}$  at 373 K  $< T < 673$  K and  $dy/dT$  is equal to  $-0.021 mN \cdot m^{-1} \cdot K^{-1}$  [7], the methaphosphate  $MPO_3$  (M = K, Rb and Cs) melts have higher values of  $\gamma$  and lower values of  $dy/dT$  due to effect of M–O ionic bonds. In isostructural crystalline orthorhombic K and Rb methaphosphates [8, 9] every cation links three polymetaphosphate chains, the cations are 8-fold coordinate, have irregular coordination polyhedra and rather wide interval of M–O bond lengths. The dispersion of corresponding bond lengths is 0.07 – 0.19 Å [8, 9], while dispersion of ionic radii is 0.12 Å. Cesium cation is about 21% larger, than  $K^+$  and have a trend to be 8-fold or higher coordinated in phosphates [10]. For high temperatures a complete dissociation of ionic M–O bonds in the melt is expected, the latter leads to significant scatter in the bonds lengths and in the cations coordination numbers. Heating increases the kinetic energy of the melt components and weakens the bonds, both ionic M–O and covalent polar P–O, decreasing  $\gamma$  values [11]. Differences in coordination and the ionic potential of cations ( $z/r$ : 0.66, 0.62 and 0.57 for 8-fold coordinate K, Rb and Cs, respectively) determine a character of the coulomb interaction weakening with the temperature increase for each of the  $MPO_3$  melts compared.

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