

Letter to Editor

SURFACE TENSION OF MOLTEN ALKALI METAPHOSPHATES

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Abstract

Two molten alkali metaphosphates (LiPO_3 and NaPO_3), known components of molten salt baths for electrolytic metallurgical processes, were examined using the ring tensiometry technique. The surface tension of the melts was measured as a function of temperature in Ar atmosphere. The surface tension decreases linearly with increasing of the temperature in the range from 1123 up to 1373 K. The surface tension data obtained were fitted by linear regression and were compared with the available literature data. The reasons of disagreement between values of surface tension taken from the literature and obtained in the present study were suggested.

Keywords: *Tensiometry; Molten salts; Thermal analysis.*

1. Introduction

Molten salt technology implemented into electrolytic metallurgical processes [1, 2] operates with electrochemical and chemical oxidation/reduction in molten salt baths. Among the molten salts, phosphates as components of molten salt bathes are frequently used for the electrowinning, electrorefining, electroplating of refractory metals and electrodeposition of the metal

coatings [3–7]. These processes are linked by the general physicochemical characteristics of molten salts that functioned as solvents. Among known literature the Janz molten salt physical properties database [8] is the most comprehensive collection of data on molten salts properties available today. For both fundamental and applied purposes lot of physicochemical properties of different melts were examined up to nowadays. However, limited data on the surface tension

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of molten alkaline metaphosphates, the latter are constituents of melts used for electroplating alloys and smooth electrodeposition of refractory metals and alloys [12, 13], are available in the literature [9–11]. So, the present work was undertaken to obtain maximal data set for the surface tensions of MPO_3 ($M = \text{Li}$ and Na) melts.

2. Experimental Details

Metaphosphate of sodium was supplied by Alfa–Aesar (NaPO_3 , 99.99%) and also was prepared by heating the Sigma-Aldrich sodium dihydrogen phosphate at 1373 K for 2 h. Metaphosphate of lithium was prepared by heating Li_2CO_3 (Aldrich, ReagentPlus TM, 99.99%) with $(\text{NH}_4)\text{H}_2\text{PO}_4$ (Aldrich, 99.999%) at 1373 K for 3 h. The atomic absorption spectrophotometry analysis of the samples with Perkin-Elmer AAS Model 603 instrument was performed to find Li or Na content. Phosphorus was analyzed by the standard vanadate-molybdate spectrophotometric method. Four analyses were done on each sample, giving results to be within ± 0.5 % of the metaphosphate composition. Differential thermal analysis (DTA) of the samples was performed under N_2 flow on samples of about 1 g using a NETZSCH STA 429 instrument. The DTA measurements were carried out at a controlled heating rate of 10 K/min. According to DTA results, LiPO_3 melts at 933 ± 1 K, which is in accordance with data [14–16], and is 10 K higher than data of [17–18]. NaPO_3 melts at 898 ± 1 K that agrees well with the melting temperature value recommended in [19] and lower than values of [16, 20, 21]. It should be noticed

that according to [22] the melting temperatures for LiPO_3 and NaPO_3 are in the ranges 911 – 939 K and 893 – 903 K, respectively.

The water content in the metaphosphates samples was found to be below 3 mass. % according to DTA data. As lowering of surface tension frequently observed for samples with high H_2O content (above 8 mass. %), so the samples were carefully heated in a shaft furnace and were remelted several times. The melts were quenched, and the glassy products were transferred into an ampoule under dynamic vacuum using the Schlenk's technique [23]. The ampoules were evacuated, sealed to prevent the water adsorption and were stored prior to surface-tension studies.

The samples obtained were remelted at 1173 K in order to measure the melt properties. The measurements of the surface tensions were carried out under excess pressure of Ar, 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 [10]. The tensiometer calibration was carried out using KCl and NaCl melts, γ values obtained are in a good agreement with those recommended in [8]. The maximum force in this study was determined exactly on the return movement of a ring. The surface tension was calculated from the following equation: $\gamma = F_{\text{max}} - F_V / (L \cdot \cos\theta)$, where γ = surface or interfacial tension; F_{max} = maximum force; F_V = weight of volume of liquid lifted; L = wetted length, θ = contact angle. The contact angle decreases as the extension increases and has the value

0° at the point of maximum force. The P content of each of metaphosphates was determined before and after surface tension runs. According to the data obtained there was no significant alteration in the M_2O/P_2O_5 ratio before and after surface-tension experiments done.

3. Results and Discussion

The data on surface tension of $LiPO_3$ melts measured by several groups of experimenters is available from the literature [24, 25]. The surface tension of melt was measured by Sokolova et al. [24] using the maximal bubble pressure method at $1028 \leq T, K \leq 1345$ and by Nijjhar and Williams [25] using the maximum pull on a cylinder method at $1030 \leq T, K \leq 1410$. These surface tension data were fitted by linear regression γ (in $mN \cdot m^{-1}$) = $a + b \cdot T(K)$ with parameters: $a = 212.2 mN \cdot m^{-1}$, $b = -0.0222 mN \cdot m^{-1} \cdot T^{-1}$ for data [24] and $a = 218.282 mN \cdot m^{-1}$, $b = -0.0241 mN \cdot m^{-1} \cdot T^{-1}$ for data [25]. The maximal bubble technique also was used by Boyer et al. [26]. The data reported in [26] can be linearized with $a = 233.88 mN \cdot m^{-1}$, $b = -0.0277 mN \cdot m^{-1} \cdot T^{-1}$ at the temperature range $959 K \leq T, K \leq 1212 K$. The data of [26] are overstated with respect to that of [24, 25]. Nowadays, the data of [24] holds as the recommended in Molten Salts Data bases [8, 27], so, the departure from the recommended values for γ reported in [25] is found to be ca. 2 %. It should be noticed that two different methods were used, their data found to be in some contradiction as one can see from the values of approximating coefficients.

The surface tension (γ) of the $LiPO_3$ melt

examined in the present study decreases with temperature and $\gamma(T, K)$ dependence shows the same linear behavior as in [24–26]. The experimental γ values measured at $1123 \leq T, K \leq 1373$ were treated by a least square regression method (l.s.r) as follows:

$$\gamma (mN \cdot m^{-1}) = 216.1 \pm 1.2 - 0.0232 \pm \pm 0.003 T / K \text{ for } LiPO_3. \quad \dots(1)$$

These data falls between those of [24] and [25] and understated with respect to those of [26].

$NaPO_3$ melts were examined by several groups of experimenters with using Du Nouÿ tensiometry [25, 28–30] and with using the maximal bubble pressure [26, 31, 32] techniques. The literature γ data was analyzed taking into account their validity and accuracy. The regression coefficients of $\gamma(T, K)$ for [25, 26, 28–32] and the temperature ranges of these studies were listed in Table 1.

The surface tension data of [31] and [32] show lowest and highest γ values among that available from the literature. The melting point of $NaPO_3$ reported in [31] is 896.5 K, which is below recommended T_m value [22], so one can suggest the presence of low-melting sodium metaphosphates in the sample content. Linear fitting of six γ values reported in [26] shows low measurements accuracy. Two set of close data with lower [25, 30] and with higher [28, 29] values of the surface tension are available.

The experimental γ values measured at $1123 \leq T, K \leq 1373$ were treated by l.s.r method as follows:

$$\gamma (mN \cdot m^{-1}) = 233.3 \pm 0.2 - 0.0451 \pm \pm 0.002 T / K \text{ for } NaPO_3 \quad \dots(2)$$

The surface tension possesses values

Table 1. The regression coefficients and the temperature range of studies

Linear regression coefficients, γ (in $\text{mN} \cdot \text{m}^{-1}$) = $a + b \cdot T$ (K)		Temperature range T , K	Ref.
a , $\text{mN} \cdot \text{m}^{-1}$	b , $\text{mN} \cdot \text{m}^{-1} \cdot \text{T}^{-1}$		
237.02	- 0.0488	1080 K – 1420 K	[25]
228.7	- 0.0398	1005 K – 1250 K	[28]
230.53	- 0.04	986 K – 1240 K	[29]
275.94	- 0.0698	1100 K – 1790 K	[32]
233.53	- 0.0492	1073 K – 1373 K	[31]
232.88	- 0.0456	1083 K – 1333 K	[30]
236.3	- 0.0453	1083 K – 1333 K	[26]

intermediate between those reported in [25, 30] and in [28, 29].

Summarizing, one can attribute the differences between γ values obtained from the tensiometric measurements to difference in purity of the sample and in density of melt; to the effect of water and gas eruptions, and to difference in the experimental methods used.

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