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THE STUDY OF SOME PHYSICO-CHEMICAL PROPERTIES OF MELT KCL – NACL MIXTURE

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Abstract

The aim of this paper was to examine the surface tension of the melt mixture of salts NaCl and KCl at temperatures 750, 800 and 850 °C by maximum bubble pressure method. Some difference between measured values of the surface tension as dependence on the method of calculation was observed. This difference results from the diameter of used capillary and does not depend on the temperature. The differences between experimentally measured values of surface tension and literary sources are trivial. The experimental results are in accordance with the literature data confirming unsuitability of maximum bubble pressure method for measurement of the melt density. The experimental result will be used as a base for the study of melt salts ternary systems. On the other side maximum bubble pressure method is the most suitable method for measurement of surface tension of melt salts, but it is unsuitable for measurement of the melt density.

Key words: salts, melt, surface tension, density, molar volumes

Introduction

Using of the mixtures of melt alkaline salts has increasing trend in the world-wide aspect, above all due to economic point of view. For example, these mixtures applied as salt flux cover during melting of aluminium alloys. The study of the physico-chemical properties of individual salts and especially of their mixture has acquired an increasing importance in recent years. The surface tension, molar volume and density are regarded as the most important physico-chemical properties of melt alkaline salts. Due to the important role played by interfacial tension in the melting of aluminum, several researchers have experimentally measured the interfacial tension of binary liquid mixtures NaCl-KCl [1-4] as well as it of ternary liquid chloride mixtures [5-7].

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The most often used methods for measurement of the surface tension are:
- stalagmometric method,
- capillary elevation method,
- maximum bubble gas pressure method.

The maximum bubble gas pressure method is the most often used method because of its simplicity, satisfactory accuracy and reproducibility. The authors of papers [6, 8-10] used this method for measurement the surface tension of binary or ternary systems of melt salts.By maximum bubble gas pressure method it is possible along with measurement of surface tension to measure also the melt density (i.e. from the values obtained at one measurement we are able to calculate besides the surface tension also the melt density) [11].

The density of melt salts mixture can be measured by several methods:
- Archimedes method,
- pycnometric method,
- dilatometric method,
- hydrostatic weighing method,
- and aforementioned maximum bubble gas pressure method [12, 13].

The Archimedes method is well known and has been successfully used to measure the densities of a large number of ionic systems [14, 15]. This method is the most precise and comparatively simple to be put into practice for high-temperature melts. A detailed consideration of the applicability of this method to high-temperature stratifying melts with limited miscibility was described in the methodological work [16]. The factors that can contribute to the error in determination density of molten salts by the Archimedes method are described in [15].

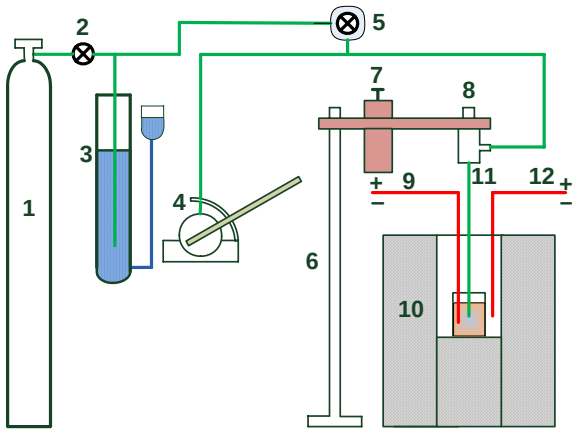


Figure 1. The layout of apparatus for determination the properties of melt salts mixture.

1. gas supply (N_2)
2. pressure control valve
3. manostat
4. micro-pressure indicator with boom pole
5. needle reduction valve
6. holder
7. mechanic shift arm
8. micro-shift
9. measuring thermocouple
10. electric resistance furnace
11. capillary
12. reducing thermocouple

Experimental

A layout of the apparatus used for measurement of the surface tension, density and molar volumes of melt mixture of KCl and NaCl is shown in Fig. 1. The nitrogen (99.5%) as inert gas was used to form the bubbles. It passed into alumina capillary with 2.486 mm in diameter. The micro-pressure indicator (manometer) UMK with boom pole was used for measuring the nitrogen pressure. The denatured ethanol was used as a measuring medium. The sensitivity of the micro-pressure indicator was controlled by the position of the boom. The salts KCl and NaCl, with the p.a. purity were obtained from LACHEMA Brno. Maximum pressure of the gas in the bubble was recorded in the moment of releasing the bubble from the tip of capillary. The immersion depth of capillary was changed five times at one measurement with device, was controlled by micrometer. The surface tension was independent of the wetting angle between the melt and capillary. The measurements were performed at 750, 800 and 850 °C at normal atmospheric conditions.

Schrödinger's equation most commonly used for calculation of the surface tension:

$$\sigma = \frac{r}{2}\left(g p_{\max.} \cdot \rho_A - g h \rho_S\right) \tag{1}$$

where:
σ – surface tension [mN/m],
r – capillary radius [m],
g – gravity acceleration [m/s^2],
$p_{max.}$ – maximum pressure - column of ethanol [m],
ρ_A – density of ethanol [kg/m^3],
h – immersion depth of capillary [m],
ρ_S – density of melt salts mixture [kg/m^3].

The density of the salt mixture can be calculated according to the equation:

$$\rho_S = \rho_A \frac{\Delta p_{\max}}{\Delta h} \tag{2}$$

where:
Δp – the difference of measured pressures,
Δh – the difference of measured depths of immersion.

Different equation was used by Matsumura et al. [8] for calculation of the surface tension according to the maximum bubble gas pressure method:

$$\sigma = r\frac{g}{2}\left[P - \rho_s\left(x + r\right)\right] \tag{3}$$

$$P = h\rho_m \tag{4}$$

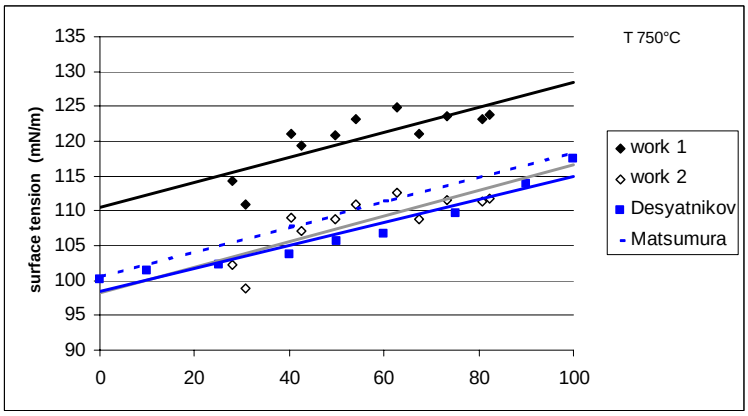
where:
σ – surface tension [mN/m],
r – capillary radius [m],

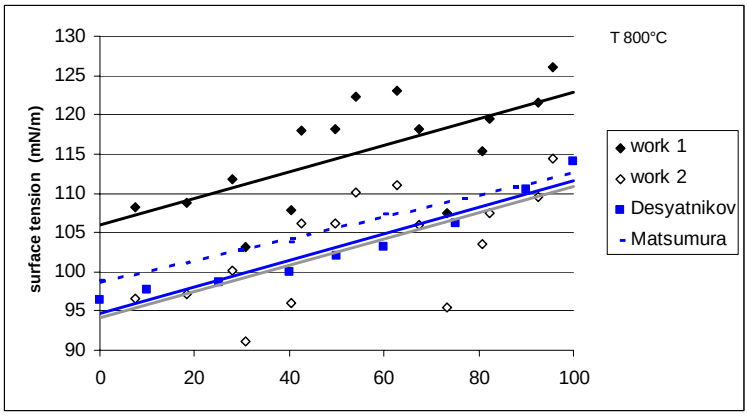
P – maximum gas pressure in the bubble [kg/m^2],
x – immersion depth of the capillary [m],
ρ_s – density of melt salt mixture [kg/m^3],
g – gravity acceleration [m/s^2],
ρ_m – density of ethanol [kg/m^3],
h – maximum pressure - column of ethanol [m].

The density of melted salts mixture can be calculated according to equation:

$$\rho_s = \frac{\Delta P}{\Delta x} \tag{5}$$

where:
ΔP – the difference of maximum pressures in the bubble,
Δx – the difference of the depths of immersion.





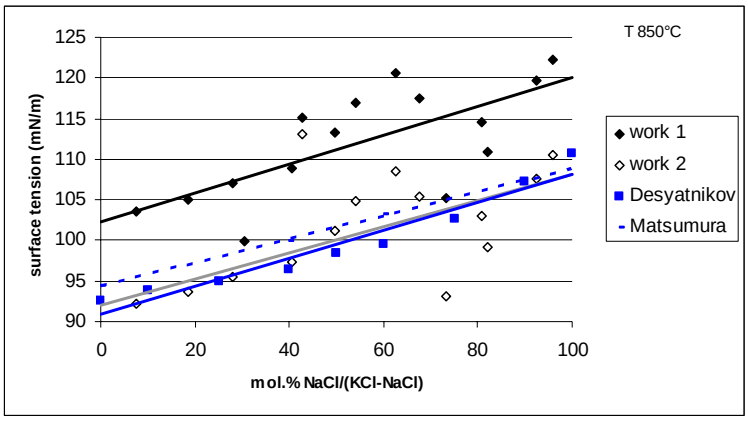


Figure 2. The influence of temperature and molar ratio of NaCl on the surface tension.

Results and discussion

The results of experiments were evaluated applying equations (1) and (3) and compared with published results [8-11]. A linear relationship between molar ratio of NaCl and the surface tension is shown in Fig. 2.

In fact, as indicated in Fig. 2, the experimentally obtained values of surface tension, calculated according to equation (1) denoted as "work 1" are higher than the values listed in the works of Janz and al., measured by Desiatnikov [9] and Matsumura [8]. Experimentally obtained values of the surface tension calculated according to equation (3) depicted in Fig. 2 as „work 2" are lower than values calculated according to equation (1). The difference between experimentally obtained values is uniform in the range between 750 and 850°C. This difference results from the radius of capillary on the right side of equation (3).

Experimentally obtained values of the surface tension calculated as „work 2" are in good agreement with results measured by Desiatnikov [9] and Fujisawu et al. [10] at molar ratio KCl – NaCl 50/50 mol % as illustrated in Fig. 3a, whereas Fig. 3b shows the plot of the density of the melt salts mixture against the temperature. The calculation of the density according to equations (2) or (5) is identical. Experimentally obtained decrease of the density with increasing temperature was more moderate in comparison with the results of Van Artsdalen and Yaffe [9, 11] or Fujisawa, Gutierrez and Toguri [10]. Van Artsdalen and Yaffe used Archimedes method.

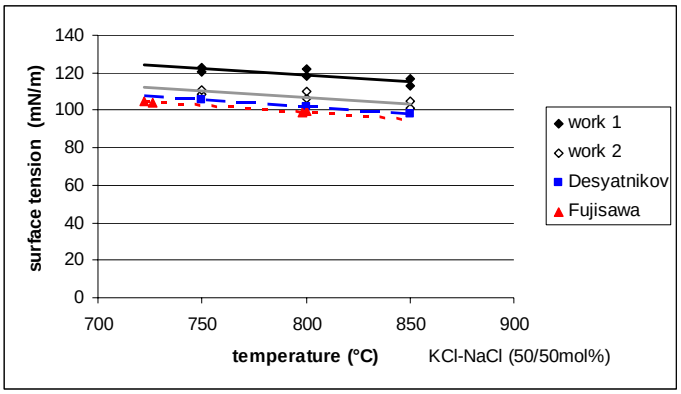


Figure 3a. The dependence of the KCl-NaCl (50/50 mol%) system surface tension on the temperature.

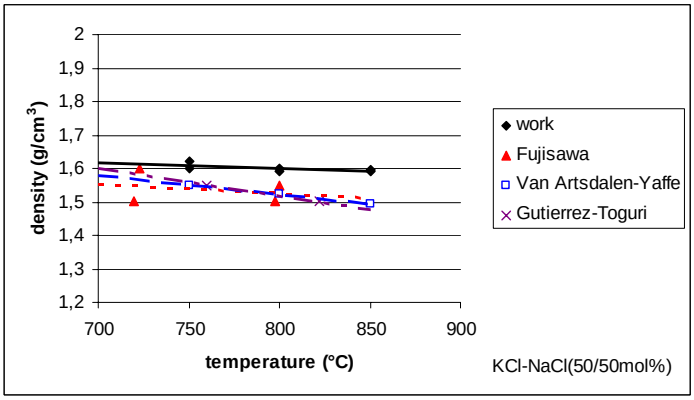


Figure 3b. The dependence of the KCl-NaCl (50/50 mol%) system density on the temperature.

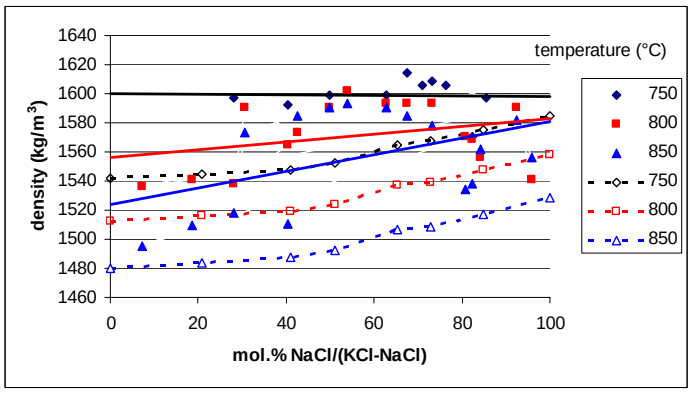


Figure 4. Dependence of density of on the molar ratio of NaCl and temperature in KCl-NaCl system.

Fig. 4 shows the influence of molar ratio of NaCl in KCl-NaCl melt salts mixture and temperature on the density. The values of density (filed graph points) experimentally obtained by maximum bubble gas pressure method were compared with values listed in the inserted table [9] (empty graph points), obtained by Archimedes method. The differences are significant. According to literary sources [9, 17-19] the maximum bubble gas pressure method is the least appropriate method for the measurement of the density of melt salts; but on the other hand it allows the same apparatus to be used (i.e. the same equipment dedicated to measurement of surface tension can be used for melt density measurement, albeit for the price of the lower accuracy).

The molar volumes for individual temperatures 750, 800 and 850°C were calculated by using measured values of density and chemical composition of the melt salts mixture. The decreasing of molar volume with increasing of NaCl molar ratio in system is shown in Fig. 5. The influence of temperature on the molar volume decreases with increasing of NaCl content.

The accuracy of measurement is affected by thickness of the wall of capillary. It is necessary to grind off its external rim of the capillary in angle-wise about 30° for up to the interior rim to minimize or more precisely eliminate the capillary wall thickness effect. Other factors, affecting the results are the accuracy of the measurement of interior diameter of capillary and the request for as perfect as possible circular section of capillary.

The maximum bubble pressure method is the most suitable method for measurement of surface tension of melt salts mixtures. It was used in more than 60 % of published works, related to binary or ternary systems. The accuracy of measurement is between 2 - 10 %, which is unsuitable for measurement of melt density. More than 70 % of works used Archimedes method for the measurement of the melt salts density with more accurate results.

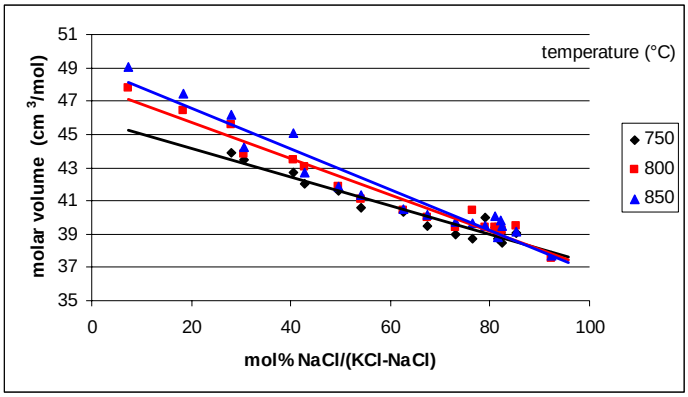


Figure 5. The influence of molar ratio of NaCl and temperature on the molar volume in KCl-NaCl system.

According to two way Analysis of Variance (ANOVA) without replication the influences of NaCl molar ratio ($p = 7.71 \cdot 10^{-18}$ for „work 1“ and $p = 0.0004213$ for „work 2“) and temperature ($p = 3.03 \cdot 10^{-14}$ for „work 1“ and $p = 3.12 \cdot 10^{-28}$ for „work 2“) have statistically significant effect on the value of surface tension. The NaCl molar ratio

($p = 3.07 \cdot 10^{-9}$) and temperature ($p = 0.001513$) have also statistically significant effect on the molar volume.

Conclusions

The values of the surface tension calculated according to equation (3) are more close to the tabular data than values calculated according to equation (1) and have less variability, as well.

The application of the maximum bubble gas pressure method to the measurement of the surface tension of the melt salts may be regarded as very satisfactory.

The Archimedes method can be successfully used to measure of the density of the melt salts. For calculation of surface tension it is advisable to use the values of density cited from literary sources.

The molar value is the linear function of the temperature. The influence of the temperature on the molar volume decreases with the increasing molar ratio of NaCl in the system.

Acknowledgements

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