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Calculation of Surface Tension of Multicomponent Silicate Solutions

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Abstract

Surface phenomena play a major role in metallurgical processes; their operation results, among others, from the surface tension of liquid oxidic systems. One of the methods of determining surface tension of oxidic systems is performing calculations with Butler's method. Surface tension was calculated for two- and three-component liquid oxidic systems typical of metallurgical processes. The determined dependence of surface tension in FeO-SiO₂ at temp. 1773 K and CaO-SiO₂ at temp. 1873 K showed that with the growing participation of SiO₂ surface tension decreased. Analogous calculations were performed for three-component systems: CaO-Al₂O₃-SiO₂ and MnO-Al₂O₃-SiO₂. The results of calculations of surface tension were determined for temp. 1873 K and compared with the results obtained by T. Tanaka et al. [19]. In both cases the increase of Al₂O₃ content resulted in a growth of surface tension. The simulation results were higher than experimental result, as compared to the literature data.

Keywords: Surface tension, Nakamoto model, CaO-Al₂O₃-SiO₂ and MnO-Al₂O₃-SiO₂ system

1. Introduction

In liquid oxidic solutions, in that metallurgic slags, the activity of a solution component depends on its interaction with the remaining components [1-5]. In the case of weak interactions the component is transported towards the surface, thus lowering the surface tension of liquid slag. The change of surface tension can be determined with the following relation [6-7]:

$$\Delta\sigma = -\frac{X_i}{kT}(m_j - m_i) \quad (1)$$

where:

X_i – molar fraction of added component,
 m_i, m_j – ionic moments of solvent j and added component i ,
 k – Boltzman constant,
 T – temperature

Ionic moment m :

$$m = \frac{ez}{r} \quad (2)$$

where:

e – electron charge,
 z – valence of ion,
 r – radius of ion.

The analysis of equations (1) and (2) reveals that ions of the added component with big radius and small charge should lower the surface tension. In the case of multicomponent oxidic solutions, the change of the surface tension is assumed to be linear when adding a component to the liquid solution. In this case the surface tension is defined with equation [8-9]:

$$\sigma = \sum_i f_i X_i \quad (3)$$

where f_i is a coefficient characteristic of each component. A significant dependence between f_i and ion potential of cation z/r coming from the oxide (fig. 1) was observed [7].

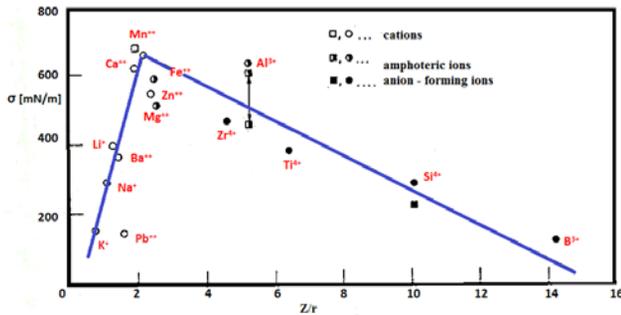


Fig. 1. Coefficient of surface tension of pure liquid metal oxides vs. their molar potentials [7]

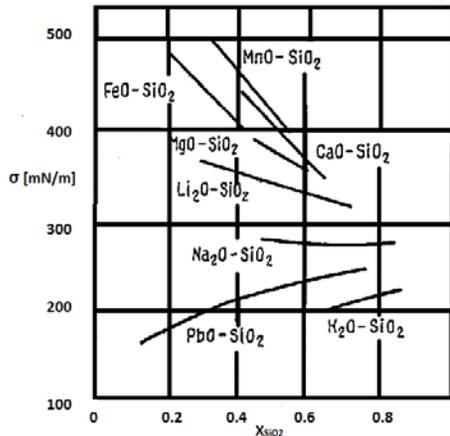


Fig. 2. Surface tension of basic silicate systems at 1500°C [7,10]

It was observed that f_i (fig.1) linearly increased for small ionic potentials with the growth of their value. After exceeding a definite value of ionic potential the surface tension decreases linearly. Ions with high ionic potential, e.g. Si, form complex anions with oxidic anions. Consequently, the value of surface tension depends on the interaction between anionic complexes and cations (with small ionic potential) and other anions.

In the case of liquid oxidic systems the surface tension equals to 0.3-0.4 N/m for acidic and 0.5-0.6 for alkaline solutions [10]. Typical silicate systems: MnO-SiO₂, CaO-SiO₂, FeO-SiO₂, MgO-SiO₂ have the highest surface tension values (fig. 2). The surface tension of bi-component liquid systems based on SiO₂ is presented in fig. 3 [10].

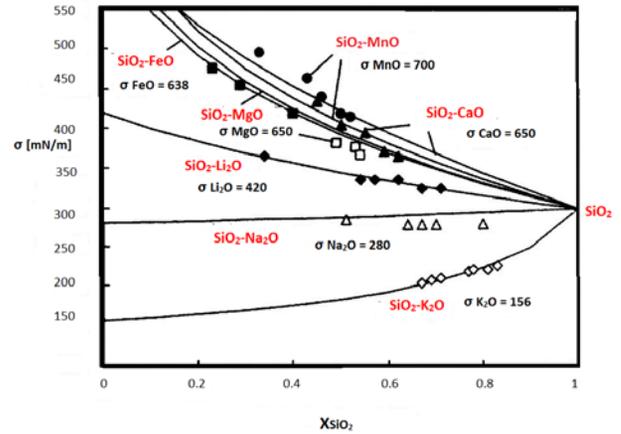


Fig. 3. Surface tension of basic silicate systems [10]

2. Thermodynamic modeling for surface tension

The Nakamoto model, based on the Butler equation for calculating surface tension of liquid oxidic solutions, was used in this paper [11-12]. It was assumed in the models that two phases can be distinguished in a liquid solution AX-BY, i.e. surface and volume phases, usually differing in their chemical composition. Unlike the Butler model where a single-molecule layer was assumed, the surface phase is at most a few molecular layers thick. The equation for a binary system in the Nakamoto model assumes the following form [12]:

$$\sigma = \sigma_{AX}^0 + \frac{R \cdot T}{A_{AX}} \cdot \ln \frac{M_{AX}^{surf}}{M_{AX}^{vol}} \quad (4)$$

$$\sigma = \sigma_{BY}^0 + \frac{R \cdot T}{A_{BY}} \cdot \ln \frac{M_{BY}^{surf}}{M_{BY}^{vol}} \quad (5)$$

where:

A, B - cations,

X, Y - anions,

σ - surface tension,

$\sigma_{AX}^0, \sigma_{BY}^0$ - surface tension of pure substances AX or BY,

A_{AX}, A_{BY} - surface means for one mole of substance in the form of a unimolecular layer (mono-molecular):

$$A_{AX} = N_0^{\frac{1}{3}} \cdot V_{AX}^{\frac{2}{3}} \quad (6)$$

N_0 - Avogadro number,

V_{AX} - molar volume AX,

$M_{AX}^{surf}, M_{AX}^{vol}$ - involved substances AX in the surface and volume phases,

defined with the formulae:

$$M_{AX}^{surf} = \frac{\frac{R_A}{R_X} \cdot N_{AX}^{surf}}{\frac{R_A}{R_X} \cdot N_{AX}^{surf} + \frac{R_B}{R_Y} \cdot N_{BY}^{surf}} \quad (7)$$

$$M_{BY}^{surf} = \frac{\frac{R_B}{R_Y} \cdot N_{BY}^{surf}}{\frac{R_A}{R_X} \cdot N_{AX}^{surf} + \frac{R_B}{R_Y} \cdot N_{BY}^{surf}} \quad (8)$$

For the volume phase [12]:

$$M_{AX}^{vol} = \frac{\frac{R_A}{R_X} \cdot N_{AX}^{vol}}{\frac{R_A}{R_X} \cdot N_{AX}^{vol} + \frac{R_B}{R_Y} \cdot N_{BY}^{vol}} \quad (9)$$

$$M_{BY}^{vol} = \frac{\frac{R_B}{R_Y} \cdot N_{BY}^{vol}}{\frac{R_A}{R_X} \cdot N_{AX}^{vol} + \frac{R_B}{R_Y} \cdot N_{BY}^{vol}} \quad (10)$$

R_A, R_B, R_X, R_Y – ionic radii of the cations and anions,

$N_{AX}^{surf}, N_{AX}^{vol}$ – mole fractions of components AX in the surface and volume phase.

The surface tension σ for a solution with a definite composition ($N_{AX}^{vol}, N_{BY}^{vol}$), where ($N_{AX}^{vol} + N_{BY}^{vol} = 1$) is defined by solving a system of three equations:

$$\sigma = \sigma_{AX}^0 + \frac{R \cdot T}{A_{AX}} \cdot \ln \frac{M_{AX}^{surf}}{M_{AX}^{vol}} \quad (11)$$

$$\sigma = \sigma_{BY}^0 + \frac{R \cdot T}{A_{BY}} \cdot \ln \frac{M_{BY}^{surf}}{M_{BY}^{vol}} \quad (12)$$

$$N_{AX}^{surf} + N_{BY}^{surf} = 1 \quad (13)$$

from which $\sigma, N_{AX}^{surf}, N_{BY}^{surf}$ are determined.

In the case of three-component systems a system of four equations has to be solved, i.e.: Butler equations for AX, BY and CZ components and an equation of balance of molar fractions of these components in the surface phase:

$$\sigma = \sigma_{CZ}^0 + \frac{R \cdot T}{A_{CZ}} \cdot \ln \frac{M_{CZ}^{surf}}{M_{CZ}^{vol}} \quad (14)$$

$$N_{AX}^{surf} + N_{BY}^{surf} + N_{CZ}^{surf} = 1 \quad (15)$$

The solution lies in defining such parameters as $N_{AX}^{surf}, N_{BY}^{surf}, N_{CZ}^{surf}$ for a given volume phase composition for which the criterial function f reaches 0. Criterial function f is defined with the following dependence:

$$f = (\sigma_{AX} - \sigma_{BY})^2 + (\sigma_{BY} - \sigma_{CZ})^2 + (\sigma_{CZ} - \sigma_{AX})^2 \quad (16)$$

3. Results of calculation

Literature abounds in the results of analytic data for surface tension in a bi-component oxidic system containing SiO_2 [13-15]. In the case of analyzed MnO-SiO_2 , some discrepancies were found between tests described in [7,14], where σ 545 erg/cm² at temp. 1873 K and 30% SiO_2 , whereas the results obtained by King [14] were higher by 10%. Analogous observations were made for σ in CaO-SiO_2 . A radical drop of σ with the increase of SiO_2 concentration was also noted. The results differed in Kojima [16], but this was due to the applied measuring method. Surface tension values for selected $\text{SiO}_2\text{-MeO}$ systems, which were determined experimentally, are presented in table 1[17]

Table 1.
Surface tension of melted silicates [17]

System	Metal oxide mol%	Temp. °C	σ mN/m
CaO-SiO ₂	35	1570	340
	55	1570	435
CaO-SiO ₂	35	1600	420
	55	1600	522
MnO-SiO ₂	50	1570	415
	70	1570	510
FeO-SiO ₂	50	1420	370
	70	1420	450
	90	1420	530

Analogously to the bi-component systems containing SiO_2 , also in FeO-MnO-SiO_2 the silicate decreases σ (fig. 4). Similar to FeO-CaO-SiO_2 , the SiO_2 component lowers σ [7]. Another important factor affecting σ value is also CaO/FeO (fig. 5). Kozakevitch [7] observed changes of σ upon adding CaO to FeO-SiO_2 (26.5%), and then FeO , which showed that σ mainly depended on the activity of SiO_2 .

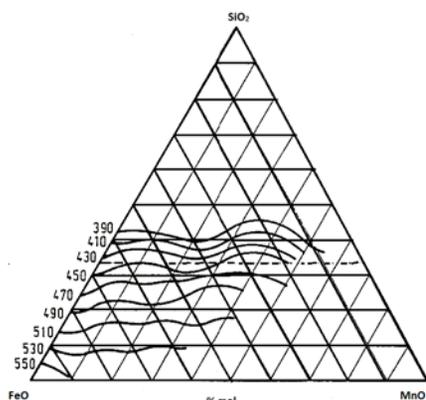


Fig. 4. Isolines of surface tension in FeO–MnO–SiO₂ at temp. 1673 K (mol%) [7, 18]

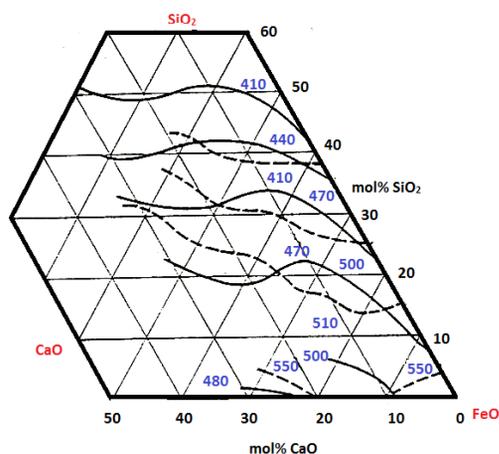


Fig. 5. Isolines of surface tension in FeO–CaO–SiO₂ at temp. 1673 K [7,18]

Data from tables 2-4 were taken into account in the calculations.

Table 2.
Values of ionic radii [12]

Si ⁴⁺	Al ³⁺	Ca ²⁺	Fe ²⁺	Mg ²⁺	Mn ²⁺	O ²⁻	SiO ₄ ⁴⁻
0.42	0.51	0.99	0.74	0.66	0.80	1.44	1.86

Table 3.
Molar volume of pure components (m³/mol) [12]

Oxide	Molar volume (m ³ /mole) vs. temperature (K)
SiO ₂	27.516 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶
Al ₂ O ₃	28.3 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶
CaO	20.7 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶
FeO	18.8 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶
MgO	16.1 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶
MnO	15.6 { 1 + 1·10 ⁻⁴ (T - 1773) } · 10 ⁻⁶

Table 4.

Parameters of the model (surface tension of pure oxides vs. temperature) [12]

Oxide	Surface tension of pure oxides (mN/m) vs. temperature (K)
Al ₂ O ₃	1024 – 0.177 T
CaO	791 – 0.0935 T
FeO	504 + 0.0984 T
MgO	1770 – 0.636 T
MnO	988 – 0.179 T
SiO ₂	243.2 + 0.031 T

Firstly, the surface tension of FeO–SiO₂ at temp. 1773 K was calculated, assuming $N_{SiO_2}^{vol}$: 0.01-0.45 (fig. 6). Analogous calculations were realized for CaO–SiO₂ at temp. 1873 K, assuming $N_{SiO_2}^{vol}$: 0.45-0.65.

The volumes of participating SiO₂ were determined after analyzing bi-component systems. They were considered to be boundary values for liquid phase occurrence in the analyzed systems. The determined dependence between surface tension and volume phase for FeO–SiO₂ at temp. 1773 K is presented in fig. 6. Its concentration range spans between pure liquid FeO and a solution containing 45 mol% SiO₂. The results indicate that with the increasing participation of SiO₂ the surface tension decreases. The total drop of surface tension in the homogeneous liquid phase equals to 33%. When the SiO₂ concentration in volume phase equals to 45 mol%, its concentration in the surface phase exceeds 80%. For comparison's sake, authors presented experimental results for temperature 1420^oC, after [17]. The values were approximately lower by about 65 mN/m.

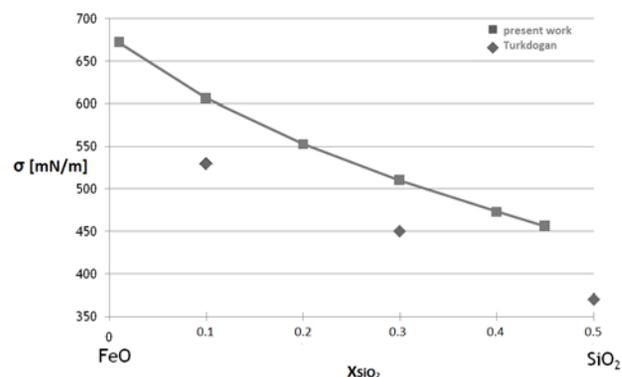


Fig. 6. Surface tension of FeO–SiO₂ at temp.1773 K

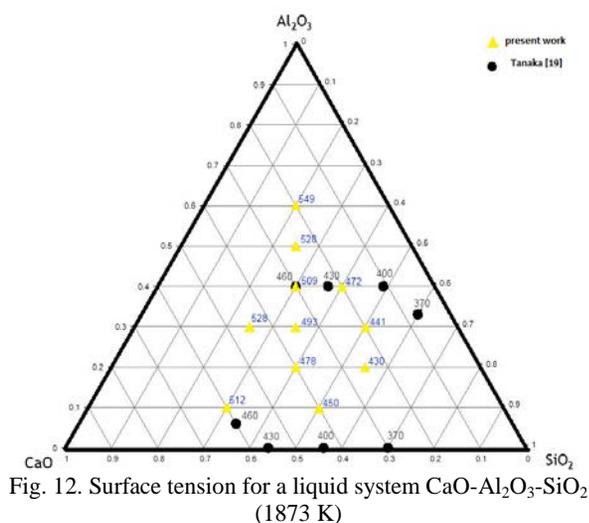


Fig. 12. Surface tension for a liquid system CaO-Al₂O₃-SiO₂ (1873 K)

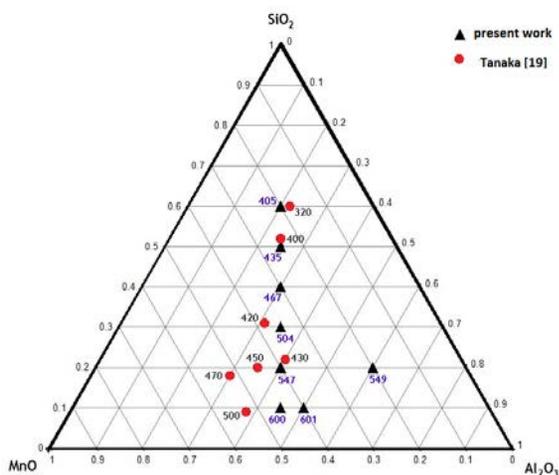


Fig. 13. Surface tension of liquid system MnO-Al₂O₃-SiO₂ (1873)

The results of calculations of surface tension (fig. 12) were determined for temp. 1873 K and compared with the results obtained by T. Tanaka et al. [19]. The calculations accounted for the slag composition with alkalinity equal to 1 and containing $X_{\text{Al}_2\text{O}_3}$ 0.1-0.4. It was also observed that the increase of SiO₂ concentration resulted in a drop of surface tension, which changes from ca. 530 to 430 mN/m. On the other hand, the increase of Al₂O₃ concentration increased the surface tension from about 450 mN/m ($X_{\text{Al}_2\text{O}_3}=0.1$) to 550 mN/m for $X_{\text{Al}_2\text{O}_3}=0.6$. The lowest surface tension value was obtained for the following solution: $X_{\text{SiO}_2}=0.55$, $X_{\text{Al}_2\text{O}_3}=0.2$, $X_{\text{CaO}}=0.25$. Where results were higher by about 50 mN/m as compared to those in Tanaka [19].

The results of calculations and experimental data on surface tension from T. Tanaka et al. [19] for MnO-Al₂O₃-SiO₂ are presented in fig. 13. The increased participation of $X_{\text{SiO}_2}=0.1-0.6$ results in a drop of surface tension from 600 to 400 mN/m, whereas the increase of $X_{\text{Al}_2\text{O}_3}$ causes an increase of surface tension. The lowest value of surface tension was obtained for $X_{\text{SiO}_2}=0.6$, $X_{\text{Al}_2\text{O}_3}=0.2$, $X_{\text{MnO}}=0.2$. The results of simulation are

higher by about 100 mN/m than the experimental data given by T. Tanaka [19].

4. Conclusions

Surface phenomena play a major role in metallurgical processes; their operation results, among others, from the surface tension of liquid oxidic systems. One of the methods of determining surface tension of oxidic systems is performing calculations with Butler's method. This method accounts for molar participation of components making up the surface liquid phase. Butler's model can be used for determining surface tension in bi- and multi-component oxidic systems whose composition is typical of metallurgical processes, without prior experimental tests. The obtained calculation results can be used for assessing the influence of particular components of liquid solution of a given phase system. It was observed for liquid FeO-SiO₂ that upon adding SiO₂ the surface tension decreased to 450 mN/m, when $X_{\text{SiO}_2}=0.45$. In the case of MnO-SiO₂ and liquid phase, surface tension lowered after SiO₂ was added. A similar regularity was observed for three-component systems: CaO-SiO₂-Al₂O₃ and MnO-Al₂O₃-SiO₂. The comparison of calculation data and experimental data reveals that experimental values are lower than those which were obtained with Butler's model.

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