

Jerzy Iwanciw*, Zofia Kalicka**, Elżbieta Kawecka-Cebula**, Krzysztof Pytel**

DETERMINATION OF THE SURFACE TENSION FOR BINARY IONIC SOLUTIONS BY MEANS OF BUTLER MODEL

1. INTRODUCTION

The Butler model equation [1] – which allows to compute the surface tension of binary and ternary solutions on the base of the surface tension data for the pure components, the excess Gibbs free enthalpy of mixing as a function of the solution composition as well as on the base of some assumptions made for the structure of the solution surface – has been used mainly for metal solutions. For such solutions the model gave usually results, which agreed well with the experimental data. The model requires some assumption as concerns the surface phase coordination number. For ionic systems like, for instance, molten salts [2] or molten oxides the application of the model is more complicated due to the ionic character of those systems. Therefore, more input data has to be used there compared to metal systems. First of all, one has to take into account the distance between ions either in the bulk and the surface phase. For that kind of systems, the Butler classic formula must be modified into the form given by [3], for instance. Another difficulty is due to the lack of reliable, high-temperature data like the specific densities, the surface tensions, the excess Gibbs free enthalpies of mixing and other specific surface parameters.

Due to the problems mentioned above, the Butler formula has been rarely applied to the molten oxides of a slag character. There, it is to report such references like two papers of Tanaka *et al.* [4] – for MnO-SiO₂ and CaO-SiO₂ systems based on the interaction parameters of the cell model and [5] – for CaO-SiO₂, FeO-Fe₂O₃, CaO-SiO₂-Fe_xO and CaO-SiO₂-Al₂O₃ systems with the thermodynamic data taken from the ChemSage data base.

In this work, a modified Butler model formula supplemented by the terms representing the thermodynamic activity coefficients of the solution components was applied. The series

* Ph.D., Faculty of Metallurgy and Materials Science, Iron Alloys Metallurgy Department, AGH University of Science and Technology, Kraków, Poland; iwanciw@metal.agh.edu.pl

** Ph.D.; D.Sc., Ass. Prof.; Ph.D., Faculty of Metallurgy and Materials Science, Heat Engineering and Environmental Protection Department, AGH University of Science and Technology, Kraków, Poland; kalicka@metal.agh.edu.pl

expansions of Ban-ya [8] and Iwanciw [9] were used. The computations were done for liquid MnO-SiO₂ system and compared to the results of [4], and subsequently for MnO-Al₂O₃ and MnO-CaO systems.

2. BUTLER MODEL

The Butler model formula for binary solutions may be given as follows

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{\gamma_A^S N_A^S}{\gamma_A^B N_A^B} = \sigma_B + \frac{RT}{A_B} \ln \frac{\gamma_B^S N_B^S}{\gamma_B^B N_B^B} \quad (1)$$

where:

- σ – the surface tension of the binary solution,
- σ_i – the surface tension of the pure component i ,
- A_i – the surface area of the monomolecular layer formed from 1 mole of the component i ,
- γ_i – the thermodynamic activity coefficient of the component i ,
- N_i – the mole fraction of the component i ,
- R, T – the gas constant and absolute temperature.

The upper index B denotes the bulk phase, while the index S – the surface phase.

The reference states for the activities are: a monomolecular layer of the pure component i for a_i^S and the bulk phase of the pure component i for a_i^B .

The surface area of 1 mole of the component i , A_i , is calculated provided a close-packed mono-layer is being formed on the surface

$$A_i = L \cdot N_A^{1/3} \cdot V_i^{2/3} \quad (2)$$

where:

- N_A – Avogadro number,
- V_i – molar volume of the pure component i ,
- L – a correction coefficient, whose numeric value depends on the structure of the surface considered and is usually set for liquid metals as 1.091.

Due to a lack of reliable data, Tanaka *et al.* [4] applied $L = 1$ for molten salts and ionic oxide solutions.

The formula (1) may be, for convenience reason, presented by a form, in which the mixing Gibbs free enthalpy is divided into its perfect solution term and the excess term

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{N_A^S}{N_A^B} + \frac{1}{A_A} \left\{ \Delta \bar{G}_A^{E,S}(T, N_B^S) - \Delta \bar{G}_A^{E,B}(T, N_B^B) \right\} = \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \left\{ \Delta \bar{G}_B^{E,S}(T, N_B^S) - \Delta \bar{G}_B^{E,B}(T, N_B^B) \right\} \end{aligned} \quad (3)$$

where $\Delta\bar{G}_i^{E,S}$ and $\Delta\bar{G}_i^{E,B}$ are the excess partial mixing Gibbs free enthalpies for the component i for the surface and the bulk phase, respectively.

As the dimensions of the ions considered differ from each other, Tanaka [2, 5] took it into account by use of the ionic distances of the substances A (d_A) and B (d_B). The ionic distance denoted by d_i , is the sum of the cation and anion radii in the considered salt or oxide.

Finally, thus modified Butler formula may be given in a form

$$\begin{aligned}\sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^S}{D_A^B} + \frac{1}{A_A} \left\{ \Delta\bar{G}_A^{E,S}(T, N_B^S) - \Delta\bar{G}_A^{E,B}(T, N_B^B) \right\} = \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^S}{D_B^B} + \frac{1}{A_B} \left\{ \Delta\bar{G}_B^{E,S}(T, N_B^S) - \Delta\bar{G}_B^{E,B}(T, N_B^B) \right\}\end{aligned}\quad (4)$$

where:

$$D_i^S = \frac{N_i^S d_i^S}{\sum N_j^S d_j^S} \quad \text{and} \quad D_i^B = \frac{N_i^B d_i^B}{\sum N_j^B d_j^B} \quad \text{for } i = A \text{ or } B.$$

3. THE EXCESS MIXING GIBBS FREE ENTHALPY IN THE SURFACE LAYER

The partial excess mixing Gibbs free enthalpies of the components A and B in the bulk phase are computed by use of the integral mixing Gibbs free enthalpy of one mole of solution, ΔG^E , as a function of the solution chemical composition. However, a similar calculation of those quantities for the surface phase requires some additional assumptions. Thus, it is assumed there, that the functional dependence of ΔG^E is identical formally for either phase, yet the numeric values of that quantity would be different for the phases in question. In other words, for the hypothetical solutions of the same chemical composition, the difference mentioned above is due only to the different coordination numbers of the phases in question as well as to the alterations of ionic distances in the surface layer resulting from relaxation effects.

By application of Lumsden's finding [6], that for the alkaline metal halides the mixing enthalpy for binaries is proportional to the potential energy of mixing coming from nonpolar London forces and the polarization energy, one may find for the partial excess mixing Gibbs free enthalpy of the component i in the bulk phase (5) the followings

$$\Delta\bar{G}_i^{E,B}(T, N_i^B) \propto \alpha Z^B (1 - N_i^B)^2 \left(\frac{z_i}{(d_i^B)^2} - \frac{z_j}{(d_j^B)^2} \right)^2 \quad (5)$$

where:

- α – polarizability,
- Z – the coordination number,
- z_i – valence of cation i ,

and for the surface phase (6)

$$\Delta\bar{G}_i^{E,S}(T, N_i^S) \propto \alpha (Z^S)' (1 - N_i^S)^2 \left(\frac{z_i}{(\zeta_i d_i^B)^2} - \frac{z_j}{(\zeta_j d_j^B)^2} \right)^2 \quad (6)$$

where:

$(Z^S)'$ – an apparent coordination number in the surface phase,
 ζ_i – the ratio of the ionic distance in the surface layer to the one in the bulk phase, i.e.,

$$\zeta_i = d_i^S / d_i^B.$$

It is to be noticed, that ignoring of either the alteration of the coordination number or the ionic distances, effected by surface relaxation, results in discrepancies between computed and experimental data.

Expression of the excess potential in the surface layer by a function of the one in the bulk allowed Choi [3] to obtain the final form of Butler model for a binary oxide solution (7)

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^S}{D_A^B} + \frac{1}{A_A} \left\{ F_{A-B}^A \cdot \Delta\bar{G}_A^{E,B}(T, N_B^S) - \Delta\bar{G}_A^{E,B}(T, N_B^B) \right\} = \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^S}{D_B^B} + \frac{1}{A_B} \left\{ F_{A-B}^B \cdot \Delta\bar{G}_B^{E,B}(T, N_B^S) - \Delta\bar{G}_B^{E,B}(T, N_B^B) \right\} \end{aligned} \quad (7)$$

where:

$$F_{i-j}^i = F_{i-j}^j = (\beta_i N_i^S + \beta_j N_j^S) \frac{\left(\frac{z_i}{(\zeta_i d_i)^2} - \frac{z_j}{(\zeta_j d_j)^2} \right)^2}{\left(\frac{z_i}{d_i^2} - \frac{z_j}{d_j^2} \right)^2} = (\beta_i N_i^S + \beta_j N_j^S) \cdot \lambda;$$

λ – the fraction defined above; it depends on the alteration of the ionic distances in the surface layer and in the bulk,

$\beta_i = (Z^S)_i' / Z_i^B$ – the alteration of the coordination number in the surface layer in comparison to the bulk.

4. DETERMINATION OF PARAMETERS β AND ζ

The ratio of the surface coordination number to the bulk one, β , is related to the evaporation enthalpy $\Delta H_{v,i}$ and to the surface tension of the considered substance σ_i by the formula [4]

$$\sigma_i A_i = (1 - \beta_i) \Delta H_{v,i} \quad (8)$$

Tanaka *et al.* [2, 4] determined the mean value of β from Eq. (8). For liquid halides of alkaline metals, it is equal to 0.94. Metal oxides exhibit usually high temperatures of melting. Their evaporation enthalpies are not known in general. They might be computed possibly as the difference between the sublimation enthalpy (if known) and the melting enthalpy at melting temperature. One may use also the empirical relationship between the evaporation enthalpy of salts and oxides and their melting temperatures, T_m , [3]

$$T_m = 5.02 \cdot 10^{-3} \Delta H_{v,i} \quad (9)$$

Coupling Eq. (8) and Eq. (9) allows to determine β from the tangent of the plot $\sigma_i = f(T_m/A_i)$. Tanaka [4] examined relationships between the surface tensions data for different liquid halides of alkaline metals, halides of bi- and tri-valent metals as well as molten metal oxides and the ratio of the melting temperature and the mole surface of the substance in question. For the all examined substances, which form liquid ionic solutions, the most adequate is the mean value of $\beta = 0.94$, which was derived from the relationship of the evaporation enthalpies of halides. Choi [3] found another β using Eq. (8) and Eq. (9). The relevant β coefficients for calcium, silicon and aluminum oxides were, respectively, 0.92; 0.94 and 0.91.

The ζ_i – parameter defined as the ratio of the ionic distances in the surface to the ones in the bulk was established theoretically for liquid sodium halide by Sawada and Nakamura [7] to be 0.97. According to Tanaka *et al.* [2] that numeric value – due to the lack of similar data for other substances – may be adequate also for the other liquid ionic solutions such as salts and metal oxides. The ζ_i – parameters found theoretically for silica, alumina and calcia are equal to, respectively, 0.9755, 0.947 and 1.008 [3].

5. CALCULATION OF THE SURFACE TENSION OF BINARY OXIDE SYSTEMS: MnO-SiO₂, MnO-CaO AND MnO-Al₂O₃

The Butler model formula, modified by Choi *et al.* [3] was applied for computation of the surface tensions of binary oxide systems: MnO-SiO₂, MnO-CaO and MnO-Al₂O₃. The essential data to make the computations are presented in Table 1.

The temperature surface tension relationships of single oxides presented in Table 1 indicate that the surface tension decreases with increasing temperature for CaO and Al₂O₃ contrary to SiO₂. As the temperature dependence of MnO surface tension was lacking, the numeric value of 630 mN/m was applied in the all calculations.

Table 1. Physicochemical data used for the computations of the surface tension of binary oxide systems: MnO-SiO₂, MnO-CaO and MnO-Al₂O₃

Oxide	V_i	σ_i	d_i^B	T_m	β_i	ζ_i
	m ³ /mol	mN/m	Å	K	–	–
CaO	$20.7 \cdot 10^{-6} [1+10^{-4}(T-1773)]$ [3]	$645.2-0.097(T-2873)$ [3]	2.4 [3]	2860	0.9242 [3]	1.008 [3]
MnO	$15.6 \cdot 10^{-6} [1+10^{-4}(T-1773)]$ [4]	630 - T_m [4] (lack of temperature expansion)	2.23	2058	0.9176 calculated from Eq. (8) and (9)	Lack of data; $\zeta_{MnO} = 1.0$ was applied
AlO _{1.5}	$14.15 \cdot 10^{-6} [1+10^{-4}(T-1773)]$ [3]	$721.2-0.078(T-2313)$ [3]	1.93 [3]	2320	0.9095 [3]	0.947
SiO ₂	$27.516 \cdot 10^{-6} [1+10^{-4}(T-1773)]$ [3]	$243.2+0.031T$ [3]	1.63 [3]	1993	0.9396 [3]	0.9755 [3]

It was decided by the authors of this work to apply different values of the coordination number ratio β_i for CaO, AlO_{1.5} and SiO₂ reported by Choi *et al.* [3], instead of the mean value 0.94 proposed by Tanaka *et al.* [2, 4]. The adequate value for MnO was calculated from Eq. (8) and Eq. (9).

The ratio of the ionic distance in the surface to the one in the bulk phase, ζ_i , was applied always as 0.97, according to Sawada [7] for the all analysed oxides. However, in the latest paper of Choi *et al.* [3], instead of the value 0.97, it was used 1.008, 0.947 and 0.9755 for, respectively, CaO, AlO_{1.5} and SiO₂. It was found that this differentiation indicates at elongation of ionic distances for CaO in the surface layer, while contraction is observed for AlO_{1.5} and SiO₂. Due to the lack of the data for MnO, the value 1 was used by the authors of this work.

The partial excess mixing Gibbs free enthalpy data for individual components of the considered solutions were those taken from Banya *et al.* [8] and Iwanciw [9] set on the base of the regular solution model.

– For MnO-SiO₂

- according to Iwanciw [9]:

$$\Delta \bar{G}_{MnO,(s)}^{E,B} = RT \ln \gamma_{MnO(s)} = -75000 \cdot N_{SiO_2}^2 + 42963 - 20 \cdot T,$$

$$\Delta \bar{G}_{SiO_2,(s)}^{E,B} = RT \ln \gamma_{SiO_2,(s)} = -75000 \cdot N_{MnO}^2 + 80000 - 30 \cdot T,$$

- according to Ban-ya [8]:

$$\Delta \bar{G}_{MnO(s)}^{E,B} = RT \ln \gamma_{MnO(s)} = -75310 \cdot N_{SiO_2}^2 - 32470 + 26.143 \cdot T,$$

$$\Delta \bar{G}_{SiO_2,(s)}^{E,B} = RT \ln \gamma_{SiO_2,(s)} = -75310 \cdot N_{MnO}^2 + 27030 - 1.983 \cdot T.$$

– For MnO-Al₂O₃

- according to Iwanciw [9]:

$$\Delta \bar{G}_{MnO(s)}^{E,B} = RT \ln \gamma_{MnO(s)} = -8000 \cdot N_{AlO_{1.5}}^2 + 42963 - 20 \cdot T,$$

$$\Delta \bar{G}_{AlO_{1.5}(s)}^{E,B} = RT \ln \gamma_{AlO_{1.5}(s)} = -8000 \cdot N_{MnO}^2 + 116208 - 50 \cdot T.$$

– For MnO-CaO

- according to Iwanciw [9]:

$$\Delta \bar{G}_{MnO(l)}^{E,B} = RT \ln \gamma_{MnO(l)} = -12000 \cdot N_{CaO}^2,$$

$$\Delta \bar{G}_{CaO(s)}^{E,B} = RT \ln \gamma_{CaO(s)} = -12000 \cdot N_{MnO}^2 + 57763 - 20 \cdot T.$$

- according to Ban-ya [8]:

$$\Delta \bar{G}_{MnO(l)}^{E,B} = RT \ln \gamma_{MnO(l)} = -92050 \cdot N_{CaO}^2 - 86860 + 51.465 \cdot T,$$

$$\Delta \bar{G}_{CaO(s)}^{E,B} = RT \ln \gamma_{CaO(s)} = -92050 \cdot N_{MnO}^2 + 18160 - 23.309 \cdot T.$$

The calculations were performed within the miscibility range of the binaries at two temperatures 1843 K and 1990 K for MnO-SiO₂ system, at 2058 K for MnO-Al₂O₃ and at 2473 K for MnO-CaO systems.

By solution of Eq. (7) the components contents in the surface layer were found, i.e., N_A^S and N_B^S (with A denoting, respectively, AlO_{1.5}, CaO or SiO₂ while B – MnO), corresponding to the components contents set for the bulk N_A^B and N_B^B .

A regression method of Newton was applied to solve Eq. (7). By denoting the differences of the right sides of Eq. (7) by $F(N_A^S, N_B^S)$, the approximated value of solution of Eq. (7) $N_{B,appr}^S$ was corrected according to Eq. (10)

$$N_B^S = N_{B,appr}^S - \frac{F(N_{A,appr}^S, N_{B,appr}^S)}{F'(N_{A,appr}^S, N_{B,appr}^S)} \quad (10)$$

where:

$N_{B,appr}^S$ – the approximated solution,

F' – the derivative related to B component, i.e., MnO in the surface phase.

For Eq. (7), the F' – derivative is given by Eq. (11)

$$F'(N_A^S, N_B^S) = \frac{RT}{N_B^S \cdot N_A^S} \left\{ \frac{D_A^S}{A_B} + \frac{D_B^S}{A_A} \right\} - \beta \cdot \lambda \cdot 2a_{AB} \left\{ \frac{N_A^S}{A_B} - \frac{N_B^S}{A_A} \right\} + \\ + \lambda (\beta_B - \beta_A) \cdot \left\{ \frac{a_{AB}(N_A^S)^2 + b_B + c_B T}{A_B} - \frac{a_{AB}(N_B^S)^2 + b_A + c_A T}{A_A} \right\} \quad (11)$$

where:

- λ and β – defined in Eq. (7);
- a_{ij} , b_i , c_i – the coefficients of the partial excess mixing Gibbs free enthalpy by the regular model approximation for i component

$$\Delta\bar{G}_i^E = RT \ln \gamma_i = a_{ij}N_j^2 + b_i + c_i \cdot T.$$

Usually, only 3 iterations are needed in order to obtain a sufficient equity of the equation sides with a desired accuracy. The found numeric data of N_B^S were used subsequently for calculations of the surface tensions for the solutions with a set MnO content. The calculated results for MnO-SiO₂ were compared to the experimental ones as well as to those of Tanaka *et al.* [4]. In his calculations Tanaka used the mean value of β for each oxide equal to 0.94 as well as the constant relaxation coefficient $\zeta = 0.97$. The numeric values of the excess functions for solution components Tanaka [4] took from the cell model.

The results of the calculations made by the authors of this work are presented in Tables 2, 3, 4 and 5 and Figures 1, 2 and 3. In the plots there are given also the miscibility gaps for the analysed systems [10].

In Table 2 and Figure 1, the computed results for MnO-SiO₂ at 1843 K are compared – following the expansions for the activity coefficients of oxides proposed in [8] and [9] – to the ones given in [4]. In Table 3 and Figure 2 are presented the calculated data for MnO-SiO₂ but at 1990 K. In Figures 2 and 3, there is not given any comparison to the experimental data as the latter are lacking.

Table 2. Comparison of calculated results for the surface tensions of molten MnO-SiO₂ mixtures at 1843 K with Tanaka's ones (assumptions: $\sigma_{\text{MnO}} = 630$ mN/m, $\sigma_{\text{SiO}_2} = 298.5$ mN/m)

Mole fraction of SiO ₂ in the bulk phase	Results calculated by Tanaka <i>et al.</i> [4]		This work, using $RT \ln \gamma_i$ relations by Ban-ya [8]		This work, using $RT \ln \gamma_i$ relations by Iwanciw [9]	
	σ	$N_{\text{SiO}_2}^S$	σ	$N_{\text{SiO}_2}^S$	σ	$N_{\text{SiO}_2}^S$
–	mN/m	–	mN/m	–	mN/m	–
0.25	–	–	–	–	502.7±2.3	0.361
0.30	505	0.362	–	–	483.6±3.2	0.393
0.35	485	0.426	471.6±3.4	0.461	466.3±1.5	0.453
0.40	561	0.518	454.9±0.7	0.501	450.3±1.2	0.493
0.43	444	0.622	446.3±4.0	0.520	440.3±2.9	0.529
0.45	–	–	439.6±1.0	0.544	435.7±3.2	0.536
0.50	–	–	425.3±2.1	0.588	422.2±4.2	0.581
0.55	–	–	411.9±2.4	0.633	–	–

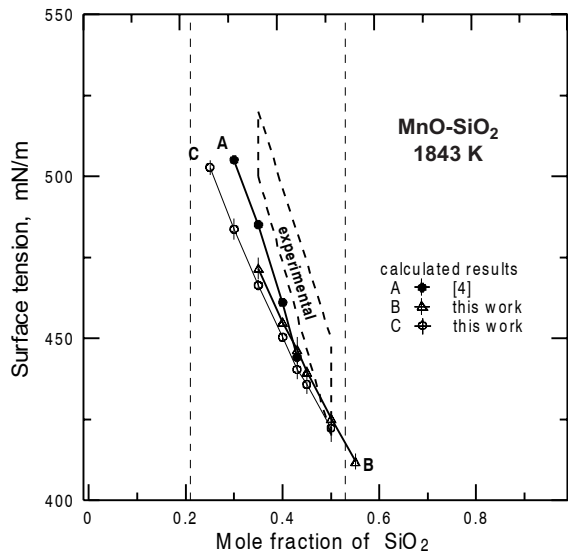


Fig. 1. Comparison of the surface tension data for liquid MnO-SiO₂ at temp. 1843 K: A – Tanaka et al. [4]; B, C – results obtained in this work with different activity coefficients expansions, “experimental” area in this drawing corresponds to the experimental data range of [4]

Table 3. Calculated results for the surface tensions of molten MnO-SiO₂ mixtures at 1990 K (assumptions: $\sigma_{\text{MnO}} = 630$ mN/m, $\sigma_{\text{SiO}_2} = 302.9$ mN/m)

Mole fraction of SiO ₂ in the bulk phase	This work, using $RT \ln \gamma_i$ relations by Ban-ya [8]		This work, using $RT \ln \gamma_i$ relations by Iwanciw [9]	
	σ	$N_{\text{SiO}_2}^S$	σ	$N_{\text{SiO}_2}^S$
–	mN/m	–	mN/m	–
0.15	–	–	543.5±2.4	0.261
0.20	–	–	520.5±1.7	0.294
0.25	–	–	500.7±1.6	0.346
0.30	–	–	482.5±1.1	0.402
0.35	–	–	465.3±3.1	0.440
0.40	459.8±2.0	0.503	448.6±2.6	0.499
0.45	444.3±0.1	0.545	433.8±0.6	0.541
0.50	429.9±1.1	0.589	420.1±0.6	0.584
0.55	416.4±1.5	0.634	407.2±1.1	0.629
0.60	–	–	395.1±1.0	0.674

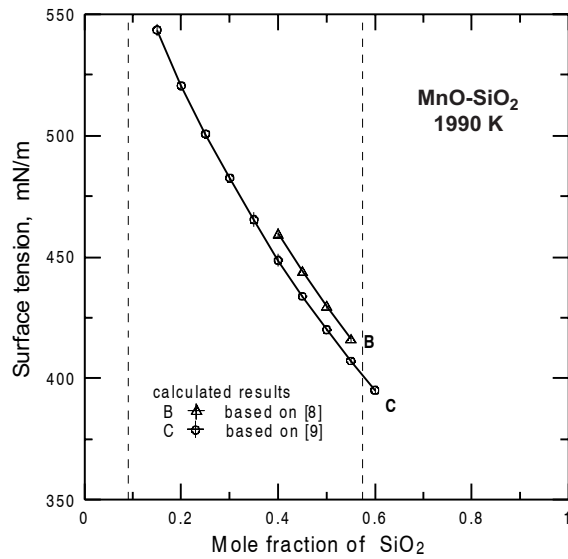


Fig. 2. Comparison of the surface tension data for liquid MnO-SiO₂ at temp. 1990 K; B, C – results obtained in this work with different activity coefficient expansions

In Table 4 and Figure 3. are presented the results for MnO-Al₂O₃ following the activity coefficient of Iwanciw [9].

Table 4. Calculated results for the surface tensions of molten MnO-Al₂O₃ mixtures at 2058 K (assumptions: $\sigma_{\text{MnO}} = 630$ mN/m, $\sigma_{\text{Al}_2\text{O}_3} = 741$ mN/m)

Mole fraction of AlO _{1.5} in the bulk phase	Mole fraction of Al ₂ O ₃ in the bulk phase	This work, using $RT \ln \gamma_i$ relations by Iwanciw [9]	
$N_{\text{AlO}_{1.5}}$	$N_{\text{Al}_2\text{O}_3}$	σ	$N_{\text{AlO}_{1.5}}^S$
–	–	mN/m	–
0.15	0.081	658.9±0.6	0.110
0.20	0.111	666.5±2.9	0.152
0.25	0.143	668.4±3.2	0.182
0.30	0.176	679±2.8	0.233
0.35	0.212	685.1±1.4	0.272
0.40	0.250	691.4±0.7	0.309
0.45	0.290	700.1±1.1	0.357
0.50	0.333	708.6±1.7	0.403

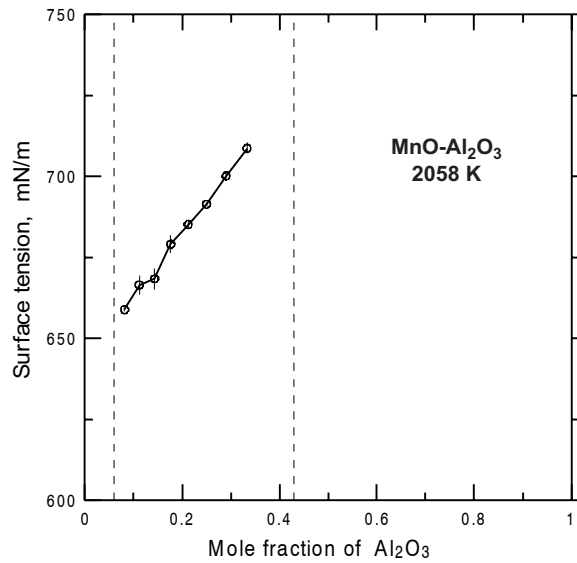


Fig. 3. The calculated surface tension data for liquid MnO- Al₂O₃ system at temp. 2058 K obtained with activity coefficients of [9]

For MnO-CaO at temp. 2473 K, the calculated results are presented in Table 5 for Iwanciw [9] expansion. The expansions of Ban-ya [8] cannot not be used in the concentration range of liquid condition. It is the most difficult system for reproduction due to very high temperature.

Table 5. Calculated results for the surface tensions of molten MnO-CaO mixtures at 2473 K (assumptions: $\sigma_{\text{MnO}} = 630$ mN/m, $\sigma_{\text{CaO}} = 684$ mN/m)

Mole fraction of CaO in the bulk phase	This work, using $RT \ln \gamma_i$ relations by Iwanciw [9]	
	σ	N_{CaO}^S
–	mN/m	–
0.10	632.6±4.1	0.083
0.15	637.2±2.3	0.128
0.20	640.6±2.2	0.173
0.25	643.6±2.8	0.217
0.30	648.6±1.3	0.272

6. CONCLUSIONS

The results obtained in this work allow for the final conclusions:

- For MnO-SiO₂ solution, the surface tensions computed by Butler model and the experimental ones agree fairly well.
- For MnO-Al₂O₃ and MnO-CaO systems, unfortunately, there is no experimentally measured surface tension data, therefore, it is not possible to make any comparison. Yet, at the moment, before any relevant research is done, the model seems to be the only real source of the surface tension data to be used for other applications.
- For metal oxide systems, the Butler approach is much more complicated and more speculative than for metal solutions. Another difficulty is still a lack of sufficient experimental surface tension data, which might be used to estimate precision of the model data. More experimental surface tension data for oxide systems are essential to make a further progress in the area of surface properties investigations.

The work was supported by Grant AGH Nr 11.11.110.555.

REFERENCES

- [1] *Butler J.V.A.*: Proc.Roy.Soc.A, **135** (1932), 348
- [2] *Ueda T., Tanaka T., Hara S.*: Z. Metallkd., **90** (1999), 342–347
- [3] *Choi J.Y., Lee H.G.*: ISIJ Int., **42** (2002), 221–228
- [4] *Tanaka T., Hach K., Iida T., Hara S.*: Z.Metallkd., **87** (1996), 380–389
- [5] *Tanaka T., Hara S.*: Z. Metallkd., **90** (1999), 348–354
- [6] *Lumsden J.*: Discussion of the Faraday Society, **32** (1961), 138 in [5]
- [7] *Sawada S., Nakamura K.*: J. Phys. C, Solid State Phys., **12** (1979), 1183 in [5]
- [8] *Ban-ya S.*: ISIJ Int., **33** (1993), 2–11
- [9] *Iwanciw J.*: Archives of Metallurgy, **49** (2004), 595–609
- [10] *Slag Atlas*, 2nd ed., VDEh, Düsseldorf, 1995

Received
April 2005