Analytical description of concentration dependence of surface tension in multicomponent systems

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Abstract. From the basic fundamental thermodynamic expressions the equation of isotherms of the surface tension of a ternary system is received. Various assumptions concerning the concentration dependence of molar areas are usually made when the equation is derived. The dependence of the molar areas is calculated as an additive function of the structure of a volumetric phase or the structure of a surface layer. To define the concentration dependence of the molar areas we used a stricter thermodynamic expression offered by Butler. In the received equation the dependence of molar areas on the structure of the solution is taken into account. Therefore, the equation can be applied for the calculation of surface tension over a wide concentration range of the components. Unlike the known expressions, the equation includes the surface tension properties of lateral binary systems, which makes the accuracy of the calculated values considerably higher. Thus, among the advantages of the offered equation we can point out the mathematical simplicity of the received equation and the fact that the equation includes physical parameters the experimental definition of which does not present any special difficulties.

1. Introduction
The research of surface properties of metals and alloys finds a wide application in solving some important scientific and technical problems, and is also widely used to solve theoretical and practical questions connected with the development of new trends in modern technology. The knowledge of the dependence of surface tension on the structure and temperatures allows to find important thermodynamic parameters.

A lot of experimental data on physical, chemical and surface properties of pure metals and binary systems have been collected by now. However, these researches are rather time-consuming. The greater the number of the components is, the more efforts the experiments demand. Therefore, a lot of attention is given to the theoretical description of the surface properties of solutions. Besides, the problem of finding stricter expressions describing the concentration dependence of the surface tension of multicomponent systems remains topical.
The existence of the proved equations for the dependence of the surface tension on the structure and temperatures will also allow predicting the adsorption phenomena in these alloys.

2. Deriving the equation of isotherms of the surface tension in multicomponent systems
Proceeding from the fundamental thermodynamic expressions by one of the authors [5] the following equation for calculating the structure of a surface layer of ideal multicomponent systems is received:

$$x_n^{\omega} = x_n - \frac{x_n(1-x_n)\omega}{RT} \left( \frac{\partial \sigma}{\partial x_n} \right)_{x_j}$$  \hspace{1cm} (1)

Where $x_n^{\omega}$ is molar fraction of $n$ component in the surface layer; $x_n$ is molar fraction of $n$ component in the volume; $\omega$ is molar area; $\sigma$ is surface tension; $R$ is universal gas constant; $T$ is temperature.

The derivative $\left( \frac{\partial \sigma}{\partial x_n} \right)_{x_j}$ is taken along the section set by the equation $\frac{x_i}{x_j} = const \ (i, j \neq m)$.

Integration of the equation (1) allows to find isotherms of the surface tension of multicomponent systems. However, the data on the dependence of molar fraction of a component in the surface layer and molar area on the structure of the solution are necessary for this purpose.

For binary systems A.I. Rusanov [4] offered to describe the dependence of molar fraction of a component on the molar fraction in the volume of a solution by the function

$$x_2^{\omega} = x_1^{\omega} = \frac{m}{x_1}$$

It is of interest to receive a similar expression for multicomponent systems. We have carried out the calculations of the structure of the surface layer of nine ternary and two four-component systems experimentally investigated in our laboratory. The received results show that the following equality exists for these systems:

$$\frac{x_n^{\omega}}{1-x_n^{\omega}} = m \frac{x_n}{1-x_n} \hspace{1cm} (2)$$

It is necessary to note that the equality (2) is valid only at the change of the structure along the cutting sections mentioned above. We shall express $x_n^{\omega}$ from (2) and substitute it into (1). Thus, irrespective of the number of the components we shall receive a differential equation:

$$d\sigma = -\frac{m-1}{1+(m-1)x_n^{\omega}} \frac{RT}{dx_n} \hspace{1cm} (3)$$

Integration of the expression (3) allows to find the dependence of surface tension on the structure of a solution. However, it is necessary to determine the functional dependence of molar area on the structure for this purpose.

Therefore, at integration of the expressions similar to (3) various assumptions concerning the concentration dependence of molar areas are made. We shall consider some.
If we assume that \( \omega = \sum_{i=1}^{n} \omega_i/n = \text{const} \) then from (3) we shall receive the expression for isotherms of the surface tension of ideal multicomponent systems.

\[
\sigma = \sigma_{n-1} - \frac{RT}{\omega} \ln \left[ 1 + x_n \left( \exp \left( \frac{\sigma_{n-1} - \sigma_n}{RT} \omega \right) - 1 \right) \right] 
\]  

(4)

Where \( \sigma_{n-1} \) is the surface tension of \( n-1 \) component of a solute.

When the structure on beam sections changes, the concentration dependence \( \omega \) can be expressed as \( \omega = \omega_{n-1} + (\omega_n - \omega_{n-1})x_n \). Then the equation (3) can be integrated without any additional assumptions for multicomponent solutions.

\[
\sigma = \sigma_{n-1} - \frac{RT(m-1)}{m \omega_{n-1} - \omega_n} \ln \left[ \frac{1 + (m-1)x_n}{\omega_{n-1} + (\omega_n - \omega_{n-1})x_n} \right] 
\]  

(5)

Where \( \omega_{n-1} \) is the molar area of \( n-1 \) component of a solute.

3. The equations of isotherms of the surface tension of a ternary system

The concentration dependence \( \omega \) can be calculated as an additive function of the structure of the surface layer \( \omega = \sum_{i=1}^{n} \omega_i x_i^\omega \). Then, integrating (3) we shall receive the equation:

\[
\sigma = \sigma_{13} - \frac{RT(m-1)}{m \omega_2 - \omega_3} \ln \left[ 1 + \left( \frac{\omega_2(m-1)}{\omega_{13}} \right)x_2 \right] 
\]  

(6)

If the concentration dependence \( \omega \) is an additive function of the structure of a volumetric phase \( \omega = \sum_{i=1}^{n} \omega_i x_i \), we shall receive the following equation:

\[
\sigma = \sigma_{12} - \frac{RT(m-1)(k+1)}{m(k \omega_1 + \omega_2) - \omega_3(k+1)} \ln \frac{(1 + (m-1)x_1)(k \omega_1 + \omega_2)}{k \omega_1 + \omega_2 - (k \omega_1 + \omega_2 - \omega_3(k+1))x_3} 
\]  

(7)

It is necessary to note that the received equations, unlike the known expressions [3, 7], include the properties of a binary solute, which considerably improves the accuracy of the surface tension calculations over the whole concentration interval.

But at the same time the above-made assumptions concerning concentration dependence of molar areas narrow the scope of application of the received equations.

Therefore, we use a stricter thermodynamic expression offered by Butler to define the concentration dependence of molar areas:

\[
\mu_i^\omega - \mu_i = \sigma \bar{\omega} 
\]  

(8)

Where \( \mu_i^\omega \) and \( \mu_i \) are chemical potentials \( i \) of a component in the surface layer and in the volume of a solution respectively; \( \bar{\omega} \) is partial molar area.
From this equation in view of the known identity \( \omega = \sum_{i=1}^{n} \omega_i x_i \), it is possible to receive the following expression for molar areas of the ideal solute:

\[
\omega = \frac{1}{\sigma} \sum_{i=1}^{n} \sigma_i \omega_i x_i^\sigma + x_i^\sigma RT \ln \frac{x_i^\sigma}{x_i}
\]  

(9)

The further reasoning is carried out for a ternary system. For this purpose we shall solve equations (3) and (9) together. Thus, on the differential equation (3) additional conditions that appear due to the concrete way of the change of the structure on beam sections are imposed. We shall assume that at the change of the structure on cutting section \( \frac{x_i}{x_y} = \text{const} \) the condition \( \frac{x_i}{x_y} = \text{const} \) satisfies. Then, having entered the designations \( \frac{x_i}{x_y} = \kappa \) and \( \frac{x_i}{x_y} = \kappa^\sigma \), we shall receive the following equation:

\[
\frac{d\sigma}{\sigma} = -\frac{(m-1)RTdx_2}{\gamma^* + (\gamma^* m - \gamma^*) + mRT \ln m} - \left(1 + (m-1)x_2 RT \ln[1 + (m-1)x_2]\right)
\]  

(10)

Where \( \gamma^* = \frac{\gamma_1^\sigma + \gamma_3^\sigma + \gamma^* mRT \ln \frac{k}{k+1} + RT \ln \frac{k+1}{k^\sigma+1}}{k^\sigma+1} \),

\( \gamma_i = \sigma_i \omega_i \) is the molar surface tension.

Integration of expression (10) is very difficult. However, the calculations done by us show that for real ternary systems the condition \( \gamma^* + (\gamma^* m - \gamma^*) + mRT \ln m \gg (1 + (m-1)x_2) RT \ln[1 + (m-1)x_2] \) satisfies. Hence, last component in the denominator (10) can be neglected. Then, integrating (10) we shall receive the expression:

\[
\sigma = \sigma_{13} \left[ \frac{\gamma^*}{\gamma^* + (\gamma^* m - \gamma^*) + mRT \ln m x_2} \right]^{\frac{(m-1)RT}{\gamma^* + (\gamma^* m - \gamma^*) + mRT \ln m}}
\]  

(11)

Where \( \sigma_{13} \) is the surface tension of the binary system 1-3.

The equation (11) at \( x_1 = 1 \) and also \( x_3 = 1 \) transforms into expressions for isotherms of a surface tension of lateral binary systems 1-2 and 2-3 respectively.

On the basis of the equation (1) calculations of \( \sigma \) for ternary systems Na-Cs-K, on sections Na:Cs = 6:1, 2:1, 1:1, 1:2, 1:6 are carried out; In-Sn-Pb, In-Sn-Ga, Tl-Pb-Bi, on section In:Sn = 9:1, 1:1, 1:9 and Tl:Pb = 9:1, 1:1, 1:9. Thus the predicted values of a surface tension except for the In-Sn-Ga system and the section Tl:Pb = 1:9 within the error of the experiment coincide with experimental data. In the ternary system In-Sn-Ga the maximum discrepancy between the calculated values and the experimental data is 5 %, and on the section Tl:Pb = 1:9 the discrepancy of 2 % is received.

Thus, the received equation (11) allows to calculate the isotherms of surface tension of ternary systems with a sufficient accuracy. The equation is relatively simple, and the calculated values will be in a much better agreement with the experimental data than those obtained with the help of the other known expressions.
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