

INTERFACIAL TENSION BETWEEN TWO LIQUID PHASES IN MOST SIMPLE TWO- AND THREE-COMPONENT SYSTEMS

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From the thermodynamic condition of equilibrium in a system located in a force field, relations were derived for calculating interfacial tensions between two pure liquids or a pure liquid phase and a binary solution provided that both phases are perfectly immiscible and the adsorption potentials depend on both the properties resp. compositions of the liquid phases and the distance from the interface. If both components of the binary solution are similar, it is possible to calculate the dependence of the interfacial tension of the solution on composition from the surface tensions and from interfacial tensions of the pure components.

The study of interfacial tension is interesting from both the theoretical and practical points of view. Phenomena at the interface of two liquid phases may be looked upon as analogs of both the surface tension and adsorption from solutions on a solid adsorbent. In this work we will derive relations for the interfacial tension for two most simple cases: a binary two-phase system composed of two pure, completely immiscible phases A and B and a ternary two-phase system, where one phase is represented by a solution of two completely miscible components A and B and the second one by pure component C.

Two Pure Completely Immiscible Liquid Phases

The system composed of two liquid phases A and B and the corresponding interface between them may be considered similarly as in the case of surface tension as a system in a force field^{1,2}. It will be assumed in this case that the interface contains two parts: the surface layer of liquid phase A and the surface layer of liquid phase B. Because it is a system containing two perfectly immiscible components, both surface layers can contain only one sort of molecules. Here, in contrast to a liquid-gas interface, the molecules in the surfacial layer of one phase are affected not only by the force field of their own bulk molecules but also by the force field due to molecules of the second phase. Under the given assumptions, the relation similar to that valid for surface tension

$$\sigma^A = \int_0^\infty \phi_A^\lambda(\varrho_A/M_A) ds, \quad (1)$$

which was derived in an earlier work^{3,4} from the thermodynamic condition of equilibrium in the force field, may be written for the interfacial tension σ_i^{A-B}

$$\sigma_i^{A-B} = \int_0^\infty \phi_B^{AB}(\varrho_A/M_A) ds + \int_0^\infty \phi_B^{AB}(\varrho_B/M_B) ds, \quad (2)$$

where ϱ_A , ϱ_B are densities, M_A , M_B molecular weights, s distance from the interface and ϕ_A^{AB} , ϕ_B^{AB} adsorption potentials acting on components A and B in a certain place of the interfacial layer AB; these potentials depend on properties of both phases. The value of ϕ_A^{AB} represents the work necessary for transferring one mol of molecules A from the bulk liquid phase A into the interface layer; ϕ_B^{AB} has a similar meaning for component B. To establish the relation between potentials ϕ_A^{AB} , ϕ_B^{AB} which determine the magnitude of the interfacial tension and potentials ϕ_A^A , ϕ_B^B which appear in equations for the surface tension, these potentials were expressed in terms of intermolecular forces. By assuming that the intermolecular forces are of central type and additive, the attractive energy between arbitrary molecule and the rest inside the bulk liquid phase is given by

$$E_{Az} = \int_{d_A}^\infty \varphi(r)_A \cdot N_A \cdot 4\pi r^2 dr, \quad (3)$$

where N_A is the number of particles in unit volume, r is the distance between centres of the interacting molecules, $\varphi(r)_A$ represents the dependence of the interaction of two molecules on the separation of their centres and d_A is the shortest distance of centres of two molecules A, from which the attractive interaction of the intermolecular forces is taken into account.

In the vicinity of the boundary, the intermolecular energy between particle A, whose centre is in distance s from this boundary, and remaining particles of phase A is given by

$$E_{As} = \int_{d_A}^s \varphi(r)_A \cdot N_A \cdot 2\pi r^2 dr + \int_s^\infty \varphi(r)_A \cdot N_A (2\pi r^2 + 2\pi r s) dr \quad (4)$$

if the distance of the centre of this particle from the boundary is greater than its diameter, $s > d$, or by

$$E_{As} = \int_d^\infty \varphi(r)_A \cdot N_A (2\pi r^2 + 2\pi r s) dr \quad (5)$$

if this distance is smaller, $s < d$.

Phase B, which is on the opposite side of the interface, interacts also with particle A.

The attractive energy between this molecule and molecules in phase B is given by the expression:

$$E_{As}^B = \int_s^\infty \varphi(r)_{AB} \cdot N_B (2\pi r^2 - 2\pi r s) dr \quad \text{for } s < d \quad (6)$$

and

$$E_{As}^B = \int_{d_{AB}}^\infty \varphi(r)_{AB} \cdot N_B (2\pi r^2 - 2\pi r s) dr \quad \text{for } s < d. \quad (7)$$

The attractive energy related to one mol of particles will be denoted from now on as ϕ_∞ and ϕ_s :

$$\phi_\infty = E_\infty \cdot N, \quad \phi_s = E_s \cdot N, \quad (8)$$

where N is Avogadro's constant.

According to its earlier definition, the adsorption potential at the interface of two liquid phases is then given by the expression:

$$\phi_A^{\Lambda-B} = (E_{As} + E_{As}^B - E_{A\infty}) = \phi_{As} + \phi_{As}^B - \phi_{A\infty} \quad (9)$$

for component A and similarly for component B. By inserting from Eqs (3)–(7) into this relation, we obtain expressions for the adsorption potential of molecules whose diameters are smaller than the distance of their centres from the interface:

$$\begin{aligned} \phi_A^{\Lambda-B} &= N \left[\int_{d_A}^s \varphi(r)_A \cdot N_A \cdot 4\pi r^2 dr + \int_s^\infty \varphi(r)_A \cdot N_A (2\pi r^2 + 2\pi r s) dr + \right. \\ &\quad \left. + \int_s^\infty \varphi(r)_{AB} \cdot N_B (2\pi r^2 - 2\pi r s) dr - \int_d^\infty \varphi(r)_A \cdot N_A \cdot 4\pi r^2 dr \right] = \\ &= N \int_s^\infty [\varphi(r)_{AB} \cdot N_B - \varphi(r)_A \cdot N_A] (2\pi r^2 - 2\pi r s) dr \quad (10) \end{aligned}$$

and for molecules whose diameters are greater than this distance:

$$\begin{aligned} \phi_A^{\Lambda-B} &= N \left[\int_{d_A}^\infty \varphi(r)_A \cdot N_A (2\pi r + 2\pi r s) dr + \right. \\ &\quad \left. + \int_{d_{AB}}^\infty \varphi(r)_{AB} \cdot N_B (2\pi r - 2\pi r s) - \right. \\ &\quad \left. - \int_{d_A}^\infty \varphi(r)_A \cdot N_A \cdot 4\pi r^2 dr \right] \end{aligned}$$

$$\begin{aligned}
&= N \left[\int_{d_{AB}}^{\infty} \varphi(r)_{AB} \cdot N_B (2\pi r^2 - 2\pi r s) dr - \right. \\
&\quad \left. - \int_{d_A}^{\infty} \varphi(r)_A \cdot N_A (2\pi r^2 - 2\pi r s) dr \right]. \quad (11)
\end{aligned}$$

The interfacial tension at the boundary of two immiscible liquid phases A and B can then be calculated from the relation

$$\begin{aligned}
\sigma_i^{A-B} &= \int_0^{\infty} (\Phi_{As} + \Phi_{Bs}^B - \Phi_{A\infty}) (\rho_A/M_A) ds + \\
&\quad + \int_0^{\infty} (\Phi_{Bs} + \Phi_{Bs}^A - \Phi_{B\infty}) (\rho_B/M_B) ds = \\
&= \int_0^{d_A} N_A \int_{d_A}^{\infty} \varphi(r)_A \cdot N_A (2\pi r s - 2\pi r^2) dr \cdot ds + \\
&\quad + \int_{d_A}^{\infty} N_A \int_s^{\infty} \varphi(r)_A \cdot N_A (2\pi r s - 2\pi r^2) dr \cdot ds + \\
&\quad + \int_0^{d_B} N_B \int_{d_B}^{\infty} \varphi(r)_B \cdot N_B (2\pi r s - 2\pi r^2) dr \cdot ds + \\
&\quad + \int_{d_B}^{\infty} N_B \int_s^{\infty} \varphi(r)_B \cdot N_B (2\pi r s - 2\pi r^2) dr \cdot ds - \\
&\quad - 2 \left[\int_0^{d_{AB}} N_A N_B \int_{d_{AB}}^{\infty} \varphi(r)_{AB} (2\pi r s - 2\pi r^2) dr \cdot ds + \right. \\
&\quad \left. + \int_{d_{AB}}^{\infty} N_A N_B \int_s^{\infty} \varphi(r)_{AB} (2\pi r s - 2\pi r^2) dr \cdot ds \right]. \quad (12)
\end{aligned}$$

As the first two terms on the rhs of this equation are identical with the expression for the surface tension of pure component⁴ A and the third and fourth terms with the expression for the surface tension of pure component B, we can write:

$$\begin{aligned}
\sigma_i^{A-B} &= \sigma^A + \sigma^B - \\
&\quad - 2 \left[\int_0^{d_{AB}} N_A N_B \int_{d_{AB}}^{\infty} \varphi(r)_{AB} (2\pi r s - 2\pi r^2) dr \cdot ds + \right. \\
&\quad \left. + \int_{d_{AB}}^{\infty} N_A N_B \int_s^{\infty} \varphi(r)_{AB} (2\pi r s - 2\pi r^2) dr \cdot ds \right]. \quad (13)
\end{aligned}$$

By assuming that the intermolecular forces can be expressed by the equation $\varphi(r) = -(A/r^6)$ and that the number of particles in unit volume N_A, N_B does not depend on the distance from the interface, it is possible to integrate and obtain an expression for the interfacial tension

$$\begin{aligned}\sigma_i^{A-B} &= \sigma^A + \sigma^B - (\pi A_{AB} N_A N_B / d_{AB}^2) = \\ &= \sigma^A + \sigma^B - 2 (A_{AB} / \sqrt{A_A A_B}) (d_A d_B / d_{AB}^2) \sqrt{(\sigma_A \sigma_B)}. \quad (14)\end{aligned}$$

This equation may be transformed to read:

$$\sigma_i^{A-B} = \sigma^A - \sigma^B \left[2 \frac{A_{AB} N_B}{A_A N_A} \left(\frac{d_A}{d_{AB}} \right)^2 - 1 \right]. \quad (15)$$

If Eqs (14) and (15) are compared with several relations for interfacial tension known from the literature, we can see that Eq. (14) passes to the Raleigh relation if $2[A_{AB}/\sqrt{(A_A A_B)}] (d_A d_B / d_{AB}^2) = 1$ or to the Girifalco and Good relation⁵ if $[A_{AB}/\sqrt{(A_A A_B)}] (d_A d_B / d_{AB}^2) = 2v_A^{1/3} \cdot v_B^{1/3} (v_A^{1/3} + v_B^{1/3})^2$ and Eq. (15) becomes identical with the Antonov's rule⁶ if $(A_{AB}/A_A) (N_B/N_A) (d_A/d_{AB})^2 = 1$.

For a water-organic compound system, we can use the Lennard-Jones potential to express the intermolecular interaction in the organic phase and the Stockmayer potential for water. Assuming that molecules of water interact with organic molecules only *via* dispersion forces independently of the molecular orientation, then, after performing integrations in Eq. (13) and neglecting the terms corresponding to repulsive intermolecular forces, we obtain the expression:

$$\sigma^{A-B} = \sigma^A + \sigma^B - 4\pi\epsilon_{AB} N_A N_B (\alpha_{AB}^6 / d_{AB}^2). \quad (16)$$

If the cross parameters ϵ_{AB} , α_{AB} and d_{AB} , are approximated by the geometric mean of the pure component parameters, it follows:

$$\sigma^{A-B} = \sigma^A + \sigma^B - 2\sqrt{\sigma_A} \sqrt{(\pi\epsilon_B \alpha_B^6 N_B^2 / d_B^2)}, \quad (17)$$

where the expression $(\pi\epsilon_B \alpha_B^6 N_B^2) / d_B^2$ is the contribution to the surface tension of water due to the existence of the dispersion forces:

$$\sigma^{A-B} = \sigma^A + \sigma^B - 2\sqrt{(\sigma_A \sigma_B^d)}. \quad (18)$$

This relation is identical with the equation proposed by Fowkes^{7,8}.

Completely Miscible Binary Solution A, B and Pure Component C

Let us have a system composed of pure liquid phase C whose surface layer contains only molecules C and solution A, B whose surface layer contains molecules A and B. Both surface layers are again the force field due to own molecules and to molecules of the second phase. From the thermodynamic condition of equilibrium in a system with a force field, the following relation has been derived for the surface tension of a solution

$$\sigma_x^{AB} = \int_{\mathfrak{g}} \{ \Phi_A^{AB} - RT \ln [x_A + (1 - x_A) \exp (\Phi_A - \Phi_B)/RT] \} Dn^{\circ}, \quad (19)$$

where x_A is the mole fraction of component A in the bulk phase, ϕ_A, ϕ_B are adsorption potentials of components A, B in a certain place of the adsorption space, Dn° is the total number of molecules in an infinitesimal volume of the surface phase and symbol $\int_{\mathfrak{g}}$ denotes the integration over the total adsorption space. If a similar relation is used for calculating the contribution of phase AB to the total interfacial tension and the contribution of phase C is expressed by a relation similar to Eq. (1), we obtain the expression for the interfacial tension σ_i^{AB-C} of the three-component system considered:

$$\begin{aligned} \sigma_i^{AB-C} = & \int_{\mathfrak{g}_{AB}} \{ \Phi_A^{AB-C} - RT \ln [x_A^{AB} + (1 - x_A^{AB}) \exp f^{AB-C}] \} Dn^{\circ} + \\ & + \int_{\mathfrak{g}_C} \Phi_C^{AB-C} Dn^{\circ}, \end{aligned} \quad (20)$$

where x_A^{AB} is the mole fraction of component A in phase AB, $f^{AB-C} = (\phi_A^{AB-C} - \phi_B^{AB-C})/RT$, $\phi_A^{AB-C}, \phi_B^{AB-C}, \phi_C^{AB-C}$ are potentials acting on components A, B, C in a certain place of the interfacial layer. These potentials depend again on properties of both phases and are equal to the work necessary for transferring 1 mol of molecules from the bulk phase to the certain place of the interfacial layer and, similarly as in the preceding case, they may be expressed by the relations

$$\Phi_A^{AB-C} = \Phi_{A_s}^{AB} + \Phi_{A_s}^C - \Phi_{A_{\infty}}^{AB} = N(E_{A_s}^{AB} + E_{A_s}^C - E_{A_{\infty}}^{AB}), \quad (21)$$

$$\Phi_B^{AB-C} = \Phi_{B_s}^{AB} + \Phi_{B_s}^C - \Phi_{B_{\infty}}^{AB} = N(E_{B_s}^{AB} + E_{B_s}^C - E_{B_{\infty}}^{AB}), \quad (22)$$

$$\Phi_C^{AB-C} = \Phi_{C_s}^{AB} + \Phi_{C_s}^C - \Phi_{C_{\infty}}^C = N(E_{C_s}^{AB} + E_{C_s}^C - E_{C_{\infty}}^C), \quad (23)$$

where $E_{A_s}^{AB}$ is the intermolecular energy between a particle of component A and

remaining molecules A and B in the interfacial layer in the distance s from the phase boundary, $E_{A_s}^C$ represents the effect of molecules of component C, which are on the second side of the phase boundary, on the molecule A considered and term $E_{A_\infty}^{AB}$ is the energy of the intermolecular interaction between molecule A and remaining particles in the bulk phase AB. Symbols $E_{B_s}^{AB}$, $E_{B_s}^C$, $E_{B_\infty}^{AB}$, $E_{C_s}^C$, $E_{C_s}^{AB}$, and $E_{C_\infty}^C$ have the similar meaning.

The energy $E_{C_s}^{AB}$ of the intermolecular interaction between particle C in the interfacial layer and molecules A and B in the solution on the second side of the boundary is given by the relation:

$$E_{C_s}^{AB} = \int_s^\infty \varphi(r)_{AC} \cdot x_A^{AB} N_{AB} (2\pi r^2 - 2\pi r s) dr + \int_s^\infty \varphi(r)_{BC} \cdot x_B^{AB} N_{AB} (2\pi r^2 - 2\pi r s) dr \quad \text{for } s > d \quad (24)$$

and

$$E_{C_s}^{AB} = \int_{d_{AC}}^\infty \varphi(r)_{AC} \cdot x_A^{AB} N_{AB} (2\pi r^2 - 2\pi r s) dr + \int_{d_{BC}}^\infty \varphi(r)_{BC} \cdot x_B^{AB} N_{AB} (2\pi r^2 - 2\pi r s) dr \quad \text{for } s < d, \quad (25)$$

where $\varphi(r)_{AC}$, $\varphi(r)_{BC}$ represent the dependence of the mutual interaction of two molecules A and C resp. B and C on the separation of their centres r , x_A^{AB} , x_B^{AB} are mole fractions of components A and B in solution AB, N_{AB} is the total number of molecules in an unit volume of the solution and d_{AC} , d_{BC} are shortest possible distances of centres of two molecules A and C resp. B and C.

If we compare relations (24) and (25) with the following expressions which represent the energy of the intermolecular interaction between particle C and molecules of pure component A resp. B on the second side of the phase boundary

$$E_{C_s}^A = \int_0^\infty \varphi(r)_{AC} N_A (2\pi r^2 - 2\pi r s) dr \quad \text{for } s > d \quad (26)$$

$$E_{C_s}^B = \int_{d_{AC}}^\infty \varphi(r)_{AC} N_A (2\pi r^2 - 2\pi r s) dr \quad \text{for } s < d \quad (27)$$

and similarly for component B, then, provided that the molar volumes of both miscible components A and B are not too different, we can write:

$$E_{C_s}^{AB} = x_A^{AB} E_{C_s}^A + x_B^{AB} E_{C_s}^B \quad (28)$$

or, after multiplying it with Avogadro's constant,

$$\phi_{C_s}^{AB} = x_A^{AB} \phi_{C_s}^A + x_B^{AB} \phi_{C_s}^B. \quad (29)$$

Inserting relations (29) and (21)–(23) into Eq. (20) we obtain:

$$\begin{aligned} \sigma_i^{AB-C} = & \int_{\mathfrak{A}_{AB}} \{ \phi_{A_s}^{AB} - \phi_{A_\infty}^{AB} + \phi_{A_s}^C - \\ & - RT \ln [x_A^{AB} + (1 - x_A^{AB}) \exp(\phi_{A_s}^{AB} - \phi_{A_\infty}^{AB} - \phi_{B_s}^{AB} - \phi_{B_\infty}^{AB})/RT] \cdot \\ & \cdot \exp(\phi_{A_s}^C - \phi_{B_s}^C)/RT \} Dn^\omega + \int_{\mathfrak{B}_C} [x_A^{AB}(\phi_{C_s}^C + \phi_{C_s}^A - \phi_{C_\infty}^C) + \\ & + x_B^{AB}(\phi_{C_s}^C + \phi_{C_s}^B - \phi_{C_\infty}^C)] Dn^\omega. \end{aligned} \quad (30)$$

Now we compare this equation with formerly derived expressions for the surface tension of pure components A and B

$$\sigma^A = \int_{\mathfrak{A}_A} (\phi_{A_s}^A - \phi_{A_\infty}^A) Dn^\omega, \quad (31)$$

$$\sigma^B = \int_{\mathfrak{B}_B} (\phi_{B_s}^B - \phi_{B_\infty}^B) Dn^\omega, \quad (32)$$

for the surface tension of solution AB:

$$\begin{aligned} \sigma^{AB} = & \int_{\mathfrak{A}_{AB}} \{ (\phi_{A_s}^{AB} - \phi_{A_\infty}^{AB}) - \\ & - RT \ln [x_A^{AB} + (1 - x_A^{AB}) \exp(\phi_{A_s}^{AB} - \phi_{A_\infty}^{AB} - \phi_{B_s}^{AB} + \phi_{B_\infty}^{AB})/RT] \} Dn^\omega \end{aligned} \quad (33)$$

and for the interfacial tension between two immiscible pure substances A–C and B–C

$$\sigma_i^{A-C} = \int_{\mathfrak{A}_A} (\phi_{A_s}^A + \phi_{A_s}^C - \phi_{A_\infty}^A) Dn^\omega + \int_{\mathfrak{B}_C} (\phi_{C_s}^C + \phi_{C_s}^A - \phi_{C_\infty}^C) Dn^\omega \quad (34)$$

$$\sigma_i^{B-C} = \int_{\mathfrak{B}_B} (\phi_{B_s}^B + \phi_{B_s}^C - \phi_{B_\infty}^B) Dn^\omega + \int_{\mathfrak{B}_C} (\phi_{C_s}^C + \phi_{C_s}^B - \phi_{C_\infty}^C) Dn^\omega. \quad (35)$$

After a rearrangement we obtain the following expression for the interfacial tension σ_i^{AB-C}

$$\begin{aligned} \sigma_i^{AB-C} = & x_A^{AB} \sigma_i^{AC} + x_B^{AB} \sigma_i^{BC} + \sigma_s^{AB} - x_A^{AB} \sigma^A - x_B^{AB} \sigma^B - \\ & - RT \int \ln [x_A^{AB} + (1 - x_A^{AB}) \exp f_A^{AB} \cdot \exp (\Phi_{As}^C - \Phi_{Bs}^C)/RT] / [x_A^{AB} + \\ & + (1 - x_A^{AB}) \exp f_A^{AB}] Dn^\omega + (1 - x_A^{AB}) \int_{\vartheta_{AB}} (\Phi_{As}^C - \Phi_{Bs}^C) Dn^\omega, \end{aligned} \quad (36)$$

where $f_A^{AB} = (\phi_{As}^{AB} - \phi_{A\infty}^{AB} - \phi_{Bs}^{AB} + \Phi_{B\infty}^{AB})/RT$. The last two terms in this equation are always of the opposite sign, their sum approaches zero if $x_A^{AB} \rightarrow 1$ and $x_A^{AB} \rightarrow 0$ and is equal to zero at an arbitrary composition of solution AB if $\phi_{As}^C = \phi_{Bs}^C$. If the intermolecular forces acting between particles A and C and particles B and C are approximately equal, we obtain a simple relation for the interfacial tension

$$\sigma_i^{AB-C} = x_A \sigma_i^{A-C} + x_B \sigma_i^{B-C} + \sigma^{AB} - x_A \sigma^A - x_B \sigma^B \quad (37)$$

which makes it possible to calculate the interfacial tension of the solution from the surface tensions of the solution and from the surface and interfacial tensions of both pure components. This assumption is fulfilled the better, the more similar are both components of the binary solution.

If a similar behaviour of both components of the solution with respect to the second phase cannot be expected, then the values of the last two terms in Eq. (33), *i.e.* K' and K'' , may be calculated from the interfacial and surface tensions of the pure components. Combining Eqs (31), (32), (34), (35) and the expression for the surface tension of pure component C:

$$\sigma^C = \int_{\vartheta_C} (\phi_{Cs}^C - \phi_{C\infty}^C) Dn^\omega \quad (38)$$

we obtain the relation

$$\int_{\vartheta_{AB}} (\Phi_{As}^C - \Phi_{Bs}^C) Dn^\omega = \frac{1}{2} [(\sigma_i^{A-C} - \sigma^A) - (\sigma_i^{B-C} - \sigma^B)]. \quad (39)$$

The value of the second term K'' is obtained directly from this equation

$$K'' = \frac{1}{2}(1 - x_A^{AB}) [(\sigma_i^{A-C} - \sigma^A) - (\sigma_i^{B-C} - \sigma^B)]. \quad (40)$$

We can calculate the value of K' if we replace f_A^{AB} , ϕ_{As}^C and ϕ_{Bs}^C by their mean values

which are constant in the whole adsorption space: then

$$K' = -\bar{n}_{AB}^{\omega} RT \ln [x_A^{AB} + (1 - x_A^{AB}) \exp \bar{f}_A^{AB} \cdot \exp (\bar{\Phi}_{As}^C - \bar{\Phi}_{Bs}^C)/RT] / [x_A^{AB} + (1 - x_A^{AB}) \exp \bar{f}_A^{AB}], \quad (41)$$

where

$$\begin{aligned} (\bar{\Phi}_{As}^C - \bar{\Phi}_{Bs}^C) &= 1/\bar{n}_{AB}^{\omega} \int_{\vartheta_{AB}} (\Phi_{As}^C - \Phi_{Bs}^C) Dn^{\omega} = \\ &= (\sigma_i^{A-C} - \sigma^A - \sigma_i^{B-C} + \sigma^B) / 2\bar{n}_{AB}^{\omega} \end{aligned} \quad (42)$$

and \bar{f}_A^{AB} may be evaluated from measured surface tensions σ^{AB} of solutions.

The derived expressions for the calculation of the interfacial tension hold under the assumption that both phases are completely immiscible; this assumption is in reality never fulfilled. This may lead to erroneous values, especially in calculations of interfacial tensions between two pure components. Even a very low value of the mutual solubility of both components in the bulk phase may result in a relatively large change of the concentration in the surface layer and, consequently, in a change of the interfacial tension.

The relations derived for the calculation of the interfacial tension in a ternary system will be verified in a next communication by a comparison with measured dependences of the interfacial tension on composition in the whole concentration range for several binary systems of the type: a binary solution of nonpolar organic substances–water.

LIST OF SYMBOLS

A_A, A_B, A_{AB}	constants of the intermolecular potential
d_A, d_B, d_{AB}	shortest distance between two molecules beyond which the attractive forces are considered
E	intermolecular energy
$b = (\phi_A - \phi_B)/RT$	
K', K''	correction terms
Dn^{ω}	number of moles in an infinitesimal volume of the surface phase
N	number of molecules of a component in unit volume
N	Avogadro's constant
r	intermolecular distance
s	distance of a molecule from the phase boundary
v	molar volume
x	mole fraction
$\alpha_A, \alpha_B, \alpha_{AB}$	parameters of the Lennard–Jones potential
$\varepsilon_A, \varepsilon_B, \varepsilon_{AB}$	parameters of the Lennard–Jones potential
ϑ	integration variable

σ	surface tension
σ_i	interfacial tension
σ^d	contribution to the surface tension due to dispersion

Subscripts

A, B, C	component
s	surface phase
ω	bulk phase

Superscripts

A, B, C, AB	phase
A-B, A-C, B-C	boundary between two pure substances
AB-C	boundary between solution AB and component C

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