A semi-empirical equation for describing the surface tension of aqueous organic liquid mixtures

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A B S T R A C T

A thermodynamic analysis is made for the dependence on composition of the surface tension showing that the latter is a mechanical thermodynamic property which is linearly related to the reciprocal of each component standard molar surface area; and that there is no simple mixing formula linking the ideal surface tension to pure-component surface tensions.

The ability of five current empirical equations to correlate the surface tension of the ideal and real binary systems water–ethanol or propan-2-ol or ethanenitrile or 1,4-dioxane at $T = 298$ K is examined. Polynomial equations are not able to describe the general, overall trend of surface tension variation across the entire composition range, where equations containing a hyperbolic term perform much better. This is the case of the proposed new equation in which two of its parameters can be estimated theoretically.

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1. Introduction

We have been developing a new approach to the thermodynamics of surface tension for planar liquid mixtures [1,2]. Basically, we took the surface phase of a pure liquid component subjected to the mixture surface tension for its standard state, designed an ideal surface phase having the same chemical composition of the corresponding real surface phase and worked out quasi-exact expressions for estimating ideal surface tensions and surface-phase compositions depending only on the knowledge of pure-component thermo-physical properties [1]. Furthermore, supported also on experimentally determined surface tensions and bulk activity coefficients, we developed a rigorous formalism to calculate activity coefficients in the surface phase of liquid mixtures [2].

Here we will show how most of the previous formalism can be expressed in terms of standard molar surface areas of the mixture constituents. Besides greater formal simplicity, the reorganised equations provide theoretical insights into the dependence of surface tension on the composition of liquid mixtures. We briefly summarise past proposals [3–5] of simple mixing rules of pure-component surface tensions to assist as reference of approximately ideal mixtures, and show that these attempts are doomed to fail because only implicit equations in the surface tension, whether ideal or real, are valid [1,6].

Building on recent work [1] leading to theoretical expressions for the limiting slopes for the dependence of surface tension on composition, we propose a new semi-empirical equation for the fit of experimental data which contains two constrained parameters. We demonstrate its good fitting ability using extensive ideal and real surface tension values of water–ethanol [7,8], water–propan-2-ol [9], water–ethanenitrile [9] and water–1,4-dioxane [10] spanning the full concentration range at $T = 298$ K, ideal values being theoretically calculated, and contrast it with the not-so-good description obtained with five different equations proposed earlier by other authors [3,11–14]. We also show that the purely empirical

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form of the proposed equation is the second best choice.

2. Surface thermodynamics of liquid mixtures. Theory

2.1. Thermodynamic context

Our approach to the chemical thermodynamics of a planar surface phase regards the latter as a separate phase at thermodynamic equilibrium with the underlying bulk phase. This formalism is also the basis of former treatments by Butler [15], Guggenheim [16], Hoar and Melford [17] and Sprow and Prausnitz [18]. However, we adopt a different view in terms of surface ideality definition, namely subjecting it to two constraints: same chemical potential of the ideal bulk phase along with identical composition to the real surface phase, conditions pictorially represented in Fig. 1.

Considering molecular substances A and B at constant temperature T and pressure p, standard states in the surface phase, denoted by superscript s, are the pure liquid components under the surface tension of the mixture at the same T and p. Hence the necessity of an expression describing the chemical potential, μ_B^*, dependence on the surface tension, γ, for a pure substance B. To this end we used Taylor's formula for a single variable around $\mu_B^*(T,p,\gamma_B^*)$ leading to $\mu_B^{0,s} = \mu_B^* + \sum_{n=1}^{\infty}[(\gamma - \gamma_B^*)^n/n!]\partial^n\mu_B^*/\partial(\gamma_B^*)^n$ and noted that $\partial^n\mu_B^*/\partial(\gamma_B^*)^n = -\partial^{(n-1)}A_B^*/\partial(\gamma_B^*)^{(n-1)}$ because $\partial\mu_B^*/\partial\gamma_B^* = -A_B^*$, where A_B^* is the molar surface area of B. Assuming pure liquid surface phase constant thickness we found that [1]:

$$\left(\frac{\partial A_B^*}{\partial \gamma_B^*}\right)_{T,p} = -\frac{A_B^*}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T \tag{1}$$

where V_B^* is the molar volume of B. At this stage we assumed, as most monolayer surface models do, that A_B^* is proportional to some power of the bulk molar volume, $A_B^* = a(V_B^*)^b$, and accordingly

$$(\partial A_B^*/\partial p)_T = -b\kappa_{T,B}^* A_B^* \tag{2}$$

where $\kappa_{T,B}^* = -(\partial V_B^*/\partial p)_T/V_B^*$ is the isothermal compressibility of B. Working out the higher order derivatives of Eq. (1) gives:

$$\left(\frac{\partial^{(n-1)}A_B^*}{\partial(\gamma_B^*)^{(n-1)}}\right)_{T,p} = (n-1)!A_B^*\left[-\frac{1}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T\right]^{(n-1)} \tag{3}$$

Introducing this expression in the Taylor's expansion and using an equation for the sum of series we arrived at Eq. (4) without any further simplification:

$$\mu_B^* - \mu_B^{0,s}(T,p,\gamma^{id}) = \frac{V_B^* A_B^*}{(\partial A_B^*/\partial p)_T}\ln\left[1 + \frac{(\gamma^{id} - \gamma_B^*)}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T\right] \tag{4}$$

Since surface and bulk ideal mixtures are at thermodynamic equilibrium, with reference to Fig. 1 we write:
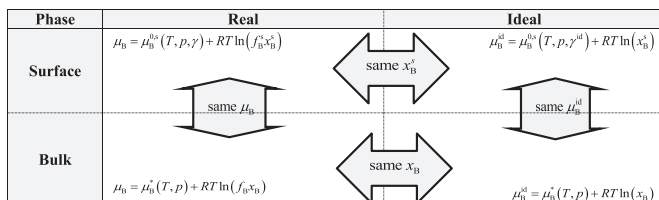

Fig. 1. Schematic thermodynamic requirements for establishing the surface ideality of a liquid mixture.

$$\mu_B^* - \mu_B^{0,s}(T,p,\gamma^{id}) = RT\ln(x_B^s/x_B) \tag{5}$$

Therefore:

$$\ln\left(\frac{x_B^s}{x_B}\right) = \frac{V_B^* A_B^*}{RT(\partial A_B^*/\partial p)_T}\ln\left[1 + \frac{(\gamma^{id} - \gamma_B^*)}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T\right] \tag{6}$$

As an analogue of Eq. (6) is valid for component A and since $x_A^s + x_B^s = 1$ in binary mixtures we find that:

$$x_A\left[1 + \frac{(\gamma^{id} - \gamma_A^*)}{V_A^*}\left(\frac{\partial A_A^*}{\partial p}\right)_T\right]^{\frac{V_A^* A_A^*}{RT(\partial A_A^*/\partial p)_T}}$$

$$+ x_B\left(1 + \frac{(\gamma^{id} - \gamma_B^*)}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T\right)^{\frac{V_B^* A_B^*}{RT(\partial A_B^*/\partial p)_T}}$$

$$= 1 \tag{7}$$

The Gibbs Adsorption Equation (GAE) for the real binary mixture may be written as [1]:

$$-\frac{A_m}{RT}\left(\frac{\partial\gamma}{\partial x_B}\right)_{T,p} = \left(\frac{x_B^s}{x_B} - \frac{x_A^s}{x_A}\right)\left[1 + x_B\left(\frac{\partial\ln f_B}{\partial x_B}\right)_{T,p}\right] \tag{8}$$

where A_m is the molar surface area and f_B is the activity coefficient of B in the bulk phase.

The corresponding ideal mixture GAE becomes [1,16,19]:

$$-\frac{A_m^{id}}{RT}\left(\frac{\partial\gamma^{id}}{\partial x_B}\right)_{T,p} = \frac{x_B^s}{x_B} - \frac{x_A^s}{x_A} \tag{9}$$

with the boundary conditions $A_m = A_m^{id} = A_A^*$ and $x_B(\partial\ln f_B/\partial x_B)_{T,p} = 0$ at $x_B = 0$; and $A_m = A_m^{id} = A_B^*$ and $x_B(\partial\ln f_B/\partial x_B)_{T,p} = 0$ at $x_B = 1$. Hence combining Eq. (7) with GAE leads to the following important results:

$$L_B^\infty = \lim_{x_B=0}\left(\frac{\partial\gamma^{id}}{\partial x_B}\right)_{T,p}$$

$$= -\frac{RT}{A_A^*}\left\{\left[1 + \frac{(\gamma_A^* - \gamma_B^*)}{V_B^*}\left(\frac{\partial A_B^*}{\partial p}\right)_T\right]^{\frac{V_B^* A_B^*}{RT(\partial A_B^*/\partial p)_T}} - 1\right\} \tag{10}$$

$$L_A^\infty = \lim_{x_B=1}\left(\frac{\partial\gamma^{id}}{\partial x_B}\right)_{T,p}$$

$$= -\frac{RT}{A_B^*}\left\{1 - \left[1 + \frac{(\gamma_B^* - \gamma_A^*)}{V_A^*}\left(\frac{\partial A_A^*}{\partial p}\right)_T\right]^{\frac{V_A^* A_A^*}{RT(\partial A_A^*/\partial p)_T}}\right\} \tag{11}$$

We note that these limiting slopes can be estimated from pure component properties and therefore can be used as constraints in empirical equations used to describe the composition dependence of mixture surface tensions.

2.2. Surface tension and molar surface area

The analogue of Eq. (4) for the real mixture is (see Fig. 1):