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Thermodynamic evaluation of molar surface area and thickness of water + ethanol mixtures

M. Soledade C.S. Santos [a,b,*], João Carlos R. Reis [b]

[a] Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[b] Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

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ABSTRACT

The molar surface area, A_m, has been a neglected property of liquid mixtures. Here its role as a surface probe over different liquid mixture regions is exposed. A thermodynamic approach to A_m calculation of planar binary liquid mixtures is developed. The relative adsorption and surface mole fraction of the surface-active component are the required input quantities. The molar surface area of thermodynamically ideal mixtures, A_m^{id}, is calculated analytically. The molar surface volume, V_m^s, is related to the bulk partial molar volumes and to the dependence of surface tensions on pressure. Thereafter the surface thickness is defined as $\tau = V_m^s/A_m$ and an approximate expression is obtained for its evaluation. The method is applied to aqueous ethanol mixtures at 298 K, using literature data and, in accordance with theoretical requirements, the variation of ideal molar surface area with surface mole fraction is not strictly linear. In the real mixture, an unexpected sharp drop in A_m is observed upon adding ethanol to water. This behaviour persists up to an ethanol-rich domain in the surface, at equilibrium with the approximately equimolar bulk mixture, then pass to larger than ideal values, reach a maximum and finally drop to the pure ethanol value. The difference $A_m - A_m^{id}$ is related to the differential enrichment of ethanol in the surface phase, defined as the difference between its equilibrium mole fractions in the surface and bulk phases. The profile for surface thickness variation with composition resembles a mirror image of A_m changes. This analysis showed that, for the largest composition difference of 0.56, $A_m - A_m^{id}$ is a minimum, $\tau - \tau^{id}$ shows a shallow maximum and the Gibbs relative adsorption of ethanol is a maximum. These findings are interpreted at a molecular level in terms of an uneven surface phase with changing thickness accompanying ethanol molecules orientation.

1. Introduction

The study of interfaces between aqueous solutions and air is of great scientific and technological importance [1]. Among the open issues in this field are the estimation of molar surfaces areas and of the surface layer thickness. Although measuring the area itself should be feasible, at least in molecular dynamics computer simulations [2], it is not easy to quantify the amount of substance and the composition near the surface region [3]. Since the thickness may be obtained by dividing the molar surface volume by the molar surface area, the question arises as to estimate molar surface volumes. These have been the basic difficulties preventing the use of molar surface areas and thicknesses for a better understanding of liquid mixture surfaces. We have been developing a thermodynamic approach to the rigorous description of planar surface phases at equilibrium with underlying bulk phases of liquid mixtures. Central to this advance is the design of an ideal surface phase with the same chemical composition of the real surface phase and at thermodynamic equilibrium with the ideal bulk phase [4]. In this way the difficult problem of determining surface-phase compositions is switched from real mixtures to the more amenable case of ideal mixtures. However, engendering a workable thermodynamic formalism to compute the molar surface area and thickness of liquid mixtures, remains a challenge which is the main goal of this paper.

On the basis of Gibbs adsorption equation [5,6] we obtain a rigorous expression to evaluate molar surface areas of liquid mixtures which, as input, uses experimental data for surface tensions and bulk activity coefficients. The molar surface volume is thermodynamically related to the partial molar volumes of the components in the bulk phase and to the pressure coefficient of the mixture surface tension. Only the thermodynamic description of the ideal surface phase requires some molecular model for estimating the molar surface areas and volumes of the pure liquid constituents. However, certain approximations were required to allow the estimation of molar surface volumes and hence surface thicknesses. We apply our method to the well investigated water + ethanol system [2–4,7–18], which is an example of an aqueous amphiphilic solution, and for which precise and extensive surface tensions [10,11], activity coefficients [19] and excess molar volumes [20] have been published. We point out the necessity of a rigorous evaluation of relative adsorptions while using Gibbs equation and suggest a robust

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* Corresponding author.
E-mail address: mssantos@ciencias.ulisboa.pt (M.S.C.S. Santos).

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method. We report and discuss some impressive findings on the variation of the molar surface area and thickness with mixture composition that strongly suggests previously unsuspected changes of surface thickness in definite composition ranges.

2. Thermodynamic basis

2.1. Gibbs adsorption equation (GAE)

Considering a homogeneous mixture of liquid substances, A and B at temperature T and pressure p, we regard the planar surface of this mixture as a thermodynamic phase in equilibrium with the underlying bulk phase. The Gibbs–Duhem equation for the surface phase is [4,21]:

$$S_{\mathrm{m}}^{\mathrm{s}}\mathrm{d}T - V_{\mathrm{m}}^{\mathrm{s}}\mathrm{d}p + A_{\mathrm{m}}\mathrm{d}\gamma + x_{\mathrm{A}}^{\mathrm{s}}\mathrm{d}\mu_{\mathrm{A}} + x_{\mathrm{B}}^{\mathrm{s}}\mathrm{d}\mu_{\mathrm{B}} = 0 \tag{1}$$

We denote the surface phase by superscript "s", a molar property of a phase by subscript "m", S is entropy, V is volume, A is surface area, γ is surface tension, $x_{\mathrm{i}}^{\mathrm{s}} = n_{\mathrm{i}}^{\mathrm{s}}/(n_{\mathrm{A}}^{\mathrm{s}} + n_{\mathrm{B}}^{\mathrm{s}})$ (n being amount of substance and i = A, B) are surface mole fractions and μ_{i} are chemical potentials. In particular, $A_{\mathrm{m}} = A/(n_{\mathrm{A}}^{\mathrm{s}} + n_{\mathrm{B}}^{\mathrm{s}})$. By convention, B is the surface-active component so that $\gamma_{\mathrm{A}}^{*} > \gamma_{\mathrm{B}}^{*}$, an asterisk indicating a pure substance property.

By dividing Eq. (1) by dx_{B} at fixed T and p and invoking the Gibbs–Duhem equation for the bulk phase we get:

$$-A_{\mathrm{m}}\left(\frac{\partial\gamma}{\partial x_{\mathrm{B}}}\right)_{T,p} = \left(x_{\mathrm{B}}^{\mathrm{s}} - \frac{x_{\mathrm{B}}x_{\mathrm{A}}^{\mathrm{s}}}{x_{\mathrm{A}}}\right)\left(\frac{\partial\mu_{\mathrm{B}}}{\partial x_{\mathrm{B}}}\right)_{T,p} \tag{2}$$

Here

$$(\partial\mu_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,p} = RT(\partial\ \ln a_{\mathrm{B}}/\partial x_{\mathrm{B}})_{T,p} \tag{3}$$

where R is the gas constant and a_{B} is the activity of B in the bulk phase. The latter is defined as the product of the rational activity coefficient of B, f_{B}, with x_B:

$$a_{\mathrm{B}} = f_{\mathrm{B}}x_{\mathrm{B}} \tag{4}$$

Gibbs' relative surface excess concentration of B with respect to A or relative adsorption of B for short, $\Gamma_{\mathrm{B}}^{(\mathrm{A})}$, is defined as [5,6,22,23]:

$$\Gamma_{\mathrm{B}}^{(\mathrm{A})} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ \ln a_{\mathrm{B}}}\right)_{T,p} = \frac{x_{\mathrm{B}}^{\mathrm{s}} - x_{\mathrm{B}}}{x_{\mathrm{A}}A_{\mathrm{m}}} \tag{5}$$

Eq. (5) is a form of the famous Gibbs adsorption equation (GAE) for a binary system, the last equality resulting from combining Eqs. (2) and (3).

In the case of thermodynamically ideal mixtures (denoted by superscript "id"), $a_{\mathrm{B}} = x_{\mathrm{B}}$($f_{\mathrm{B}} = 1$) at every composition and Eq. (5) becomes:

$$\Gamma_{\mathrm{B}}^{(\mathrm{A})\mathrm{id}} = -\frac{1}{RT}\left(\frac{\partial\gamma^{\mathrm{id}}}{\partial\ \ln x_{\mathrm{B}}}\right)_{T,p} = \frac{x_{\mathrm{B}}^{\mathrm{s}} - x_{\mathrm{B}}}{x_{\mathrm{A}}A_{\mathrm{m}}^{\mathrm{id}}} \tag{6}$$

It is appropriate to digress here to show how $x_{\mathrm{B}}^{\mathrm{s}}$ and γ^{id} can be rigorously evaluated. We have designed an ideal surface phase [4] that is in thermodynamic equilibrium with the underlying ideal bulk phase while having the same composition as the real surface phase. Consequently, $x_{\mathrm{B}}^{\mathrm{s}}$ can be determined using ideal mixing thermodynamics. This has been done before [4] on the assumption of constant thickness for the surface phase of pure liquids at fixed T and p. We have improved this treatment by removing this constraint and a full derivation of the thermodynamic link between $x_{\mathrm{B}}^{\mathrm{s}}$ and x_{B} is now presented in Appendix A. Estimates of molar surface area for the pure components are made using the anisotropic surface model [4,24]. According to this model, the surface-phase molar volume of B, $V_{\mathrm{B}}^{*,\mathrm{s}}$, is given by:

$$V_{\mathrm{B}}^{*,\mathrm{s}} = \left(V_{\mathrm{c,B}}^{*}/V_{\mathrm{B}}^{*}\right)^{3/5}V_{\mathrm{B}}^{*} \tag{7}$$

where $V_{\mathrm{c,\ B}}^{*}$ is the critical molar volume. Considering a monolayer with cubic arrangement, the molar surface area A_{B}^{*} becomes:

$$A_{\mathrm{B}}^{*} = L^{1/3}\left(V_{\mathrm{c,B}}^{*}\right)^{6/15}\left(V_{\mathrm{B}}^{*}\right)^{4/15} \tag{8}$$

and its pressure coefficient is:

$$\left(\partial A_{\mathrm{B}}^{*}/\partial p\right)_{T} = -(4/15)A_{\mathrm{B}}^{*}\kappa_{T,\mathrm{B}}^{*} \tag{9}$$

Here L is the Avogadro constant and $\kappa_{T,\ \mathrm{B}}^{*}$ is the isothermal compressibility of B. The resulting Eq. (A.24) can be written as:

$$\ln\frac{x_{\mathrm{B}}^{\mathrm{s}}}{x_{\mathrm{B}}} = \frac{A_{\mathrm{B}}^{*}\ Q_{\mathrm{B}}^{*}}{RT}\ \ln\left(1 + \frac{\gamma^{\mathrm{id}} - \gamma_{\mathrm{B}}^{*}}{Q_{\mathrm{B}}^{*}}\right) \tag{10}$$

where the short-hand Q_{B}^{*} stands for:

$$Q_{\mathrm{B}}^{*} = \frac{\left(1 + V_{\mathrm{B}}^{*,\mathrm{s}}/2V_{\mathrm{B}}^{*}\right)V_{\mathrm{B}}^{*}}{\left(\partial A_{\mathrm{B}}^{*}/\partial p\right)_{T}} \tag{11}$$

and similarly, for Q_{A}^{*}.

Since an analogous equation holds for constituent A and since $x_{\mathrm{A}}^{\mathrm{s}} + x_{\mathrm{B}}^{\mathrm{s}} = 1$, the ideal surface tension γ^{id} can be calculated by solving the following non-explicit equation:

$$x_{\mathrm{A}}\left[1 + \left(\gamma^{\mathrm{id}} - \gamma_{\mathrm{A}}^{*}\right)/Q_{\mathrm{A}}^{*}\right]^{Q_{\mathrm{A}}^{*}A_{\mathrm{A}}^{*}/RT} + x_{\mathrm{B}}\left[1 + \left(\gamma^{\mathrm{id}} - \gamma_{\mathrm{B}}^{*}\right)/Q_{\mathrm{B}}^{*}\right]^{Q_{\mathrm{B}}^{*}A_{\mathrm{B}}^{*}/RT} = 1 \tag{12}$$

Differentiation of Eq. (12) yields the following expression for the analytic calculation of $\Gamma_{\mathrm{B}}^{(\mathrm{A})\mathrm{id}}$:

$$\begin{aligned}\Gamma_{\mathrm{B}}^{(\mathrm{A})\mathrm{id}} &= -\frac{1}{RT}\left(\frac{\partial\gamma^{\mathrm{id}}}{\partial\ \ln x_{\mathrm{B}}}\right)_{T,p}\\ &= \frac{x_{\mathrm{B}}^{\mathrm{s}} - x_{\mathrm{B}}}{x_{\mathrm{A}}}\Big/\left(\frac{x_{\mathrm{A}}^{\mathrm{s}}A_{\mathrm{A}}^{*}}{1 + (\gamma^{\mathrm{id}} - \gamma_{\mathrm{A}}^{*})/Q_{\mathrm{A}}^{*}} + \frac{x_{\mathrm{B}}^{\mathrm{s}}A_{\mathrm{B}}^{*}}{1 + (\gamma^{\mathrm{id}} - \gamma_{\mathrm{B}}^{*})/Q_{\mathrm{B}}^{*}}\right)\end{aligned} \tag{13}$$

Returning to GAE, to study the phenomenology of the relative adsorption of B as a function of the mixture composition, we enquire into the boundary values of $\Gamma_{\mathrm{B}}^{(\mathrm{A})}$ and $(\partial\Gamma_{\mathrm{B}}^{(\mathrm{A})}/\partial x_{\mathrm{B}})_{T,\ p}$. At $x_B = 0$ there are no surface-active molecules in the surface phase ($x_{\mathrm{B}}^{\mathrm{s}} = 0$) and Eq. (5) gives the following known result:

$$\lim_{x_{\mathrm{B}}=0}\Gamma_{\mathrm{B}}^{(\mathrm{A})} = 0 \tag{14}$$

However, at the other composition boundary ($x_{\mathrm{B}} = 1$) Eq. (5) becomes a type 0/0 indeterminate. Turning for aid to L'Hôpital's rule, we write (with all derivatives taken at fixed T and p):

$$\lim_{x_{\mathrm{B}}=1}\Gamma_{\mathrm{B}}^{(\mathrm{A})} = \frac{\lim\limits_{x_{\mathrm{B}}=1}\left(\dfrac{\partial x_{\mathrm{B}}^{\mathrm{s}}}{\partial x_{\mathrm{B}}}\right) - 1}{\lim\limits_{x_{\mathrm{B}}=1}\left(x_{\mathrm{A}}\dfrac{\partial A_{\mathrm{m}}}{\partial x_{\mathrm{B}}} - A_{\mathrm{m}}\right)} \tag{15}$$

Differentiation of Eq. (10) gives:

$$\frac{\partial x_{\mathrm{B}}^{\mathrm{s}}}{\partial x_{\mathrm{B}}} = \frac{x_{\mathrm{B}}^{\mathrm{s}}}{x_{\mathrm{B}}}\left[1 + \frac{x_{\mathrm{B}}A_{\mathrm{B}}^{*}}{RT\left(1 + (\gamma^{\mathrm{id}} - \gamma_{\mathrm{B}}^{*})/Q_{\mathrm{B}}^{*}\right)}\frac{\partial\gamma^{\mathrm{id}}}{\partial x_{\mathrm{B}}}\right] \tag{16}$$