Interpretation of adsorption excess quantities: the absolute surface excess concentration

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Abstract: The concept of absolute surface excess of adsorption accounts for the expansion of compression of the volume of a pure liquid under the influence of a solid surface. The absolute surface excess amount of substance can prove to be a powerful measure of the adsorption at a solid/binary liquid interface, too. The contributions of the composition and volumetric effects to the adsorption can be separated from each other in this concept, and both of them are experimentally accessible quantities.

Key words: Adsorption excess quantities; Gibbs dividing surface; solid-liquid interface

Introduction

The most frequently used measures of the adsorption from a solution onto a solid surface are the molar reduced (n\text{\scriptsize{r}}(\alpha)) and, in certain cases, the volumetric reduced (n\text{\scriptsize{V}}(\alpha)) excess amount of substance [1]. They have a property in common: their values become zero in pure liquids, because they are related to the difference in the liquid composition before and after the adsorption equilibrium. Findenegg et al. measured the excess masses of pure liquids in contact with solid surfaces by high-precision pyknometric and dilatometric techniques [2-7]. For instance, in the case of Graphite as the adsorbent, the excess mass of water in the interfacial region was found to be negative [2], while the excess masses of long-chain alcohols at the Graphite surface were positive [4,5]. The temperature-dependences of the excess masses (the adsorption isobars) of pure liquids at solid surfaces gave considerable information about the structure of the interfacial layer. Some inferences drawn from such adsorption data were confirmed in heat of immersion experiments [8]. In this work, we point to the fact that the excess mass in Findenegg’s experiments is an “absolute surface excess” quantity, as it was termed originally by Wang et al. [9]. In a previous paper, algebraic and geometric interpretations were given for the various adsorption excess quantities in solid/binary liquid systems [1]. These considerations will be extended here to the special case of pure liquids.

Theory

If a solid adsorbent is immersed in a pure liquid, a two-phase two-component system is obtained. The superscripts \(\alpha\) and \(\beta\) denote the liquid phase and the solid phase, respectively, and the subscripts 1 and 2 the liquid and solid components, respectively. Following the algebraic considerations in [1], the excess volume \(V^\alpha\) of the system and the excess amount \(n_i^\alpha\) of the i-th substance in the system can be defined relative to a reference system as

\[ V^\alpha = V - \lambda^\alpha - \lambda^\beta, \]

\[ n_i^\alpha = n_i^0 - \lambda^\alpha c_i^\alpha - \lambda^\beta c_i^\beta, \quad i = 1, 2, \]

where \(V\) is the equilibrium volume of the system, \(n_i^0\) is the total number of moles of the i-th component in the system, and \(c_i^\alpha\) and \(c_i^\beta\) denote the equilibrium mole concentrations of the i-th species in the bulk phases \(\alpha\) and \(\beta\). The quantities \(\lambda^\alpha\) and \(\lambda^\beta\) are reference volumes, the magnitudes of which can be chosen arbitrarily with the main feature that the intensive properties (e.g., concentrations) of these reference
volumes are the same as the intensive properties of the corresponding bulk phases of the real system. The total volume of the reference system is \( V_0 = \lambda^a + 2 \beta \). The total volume of the real system in the equilibrium state is the sum of the equilibrium volumes of the two-phases: \( V = V^a + V^b \). Usually, a rigid adsorbent is completely insoluble in the liquid and the liquid cannot interpenetrate the interior of the adsorbent: \( c^a = c^b = 0 \). Furthermore, it is reasonable to assume that the initial volume of the solid, \( V^\beta_0 \), does not change after equilibration: \( V^\beta = V^\beta_0 \). The liquid volume, however, is easily perturbed by the solid, i.e., dilatation (\( V^a > V^a_0 \)) or contraction (\( V^a < V^a_0 \)) can occur under the influence of the solid surface. The “adsorption” is said to be isochoric if the liquid volume remains unchanged: \( V^a = V^a_0 \). To obtain a well-defined measure of the adsorption of the pure liquid (component 1), \( \lambda^a \) and \( \beta^b \) should be chosen to make \( n^a \) the experimental quantity. We may choose \( \lambda^a = V^a \) and \( \beta^b = V^b \), i.e., the reference system has the same volume and subvolumes as the real system. Taking all these considerations into account, the excess volume of the system becomes zero (\( V^\sigma = 0 \)), and the excess amount of the solid component also becomes zero (\( n^\beta = 0 \)). The excess amount of the liquid component, however, usually differs from zero:

\[
n^a_1 = n^\text{ASEC}_a = n^a_0 - V^a c^a, \tag{3}
\]

where \( n^\text{ASEC}_a \) (absolute surface excess concentration, ASE)} is the excess of the liquid in the real system relative to the particular reference system. Using the superscript \( l \) instead of \( \sigma \) and ignoring subscript 1, Eq. (3) can be rewritten as:

\[
n^l_\sigma = n^\text{ASEC}_\sigma = c^\sigma V^\sigma - c^l V^l, \tag{4}
\]

where \( n^l_\sigma \) is the excess amount of the Findenegg type and is identical with \( n^\text{ASEC}_\sigma \). A more familiar expression is obtained when Eq. (4) is rewritten by using the liquid density:

\[
m^l_\sigma = m^\text{ASEC}_\sigma = \rho^\sigma V^\sigma - \rho^l V^l = \rho^\sigma (V^\sigma - V^l), \tag{5}
\]

since \( \rho^l = \rho^\sigma \) for a pure liquid. Thus, the excess mass \( (m^l_\sigma) \) can be determined by measuring the liquid volume before and after equilibration. (In experimental work, one has to face the problem that the excess mass of any liquid can be determined only relative to a reference liquid [2,3]. In principle, the reference liquid should be chosen to give isochoric “adsorption” (\( m^l_\sigma = 0 \)) onto the solid under investigation. As a result of the solid-liquid interaction, the adsorption is positive if contraction (\( V^l < V^\sigma \)) occurs, and negative if dilatation (\( V^l > V^\sigma \)) takes place. The excess mass of a pure liquid is zero under isochoric conditions (\( V^l = V^\sigma \)), in contrast with binary liquids, where the composition change leads to a surface excess different from zero, even if the adsorption is isochoric. It is worth mentioning that, as a first approximation, the difference \( V^\sigma - V^l \) in Eq. (5) has nothing to do with the volume (\( V^\sigma \)) of the adsorption layer. The latter is the difference between the total volume of the liquid after equilibration and the maximum volume of the liquid which can still be regarded as homogeneous: \( V^\sigma = V^l - V^b \) (here, the superscript \( b \) would be more correct than \( 1 \) to refer to the density and concentrations in the bulk liquid). Clearly, \( V^\sigma \) is not a direct experimental quantity. A geometric representation of the absolute excess mass is given by a simple cylindrical arrangement in Fig. 1, which shows the density distributions of a pure liquid at three solid surfaces of different kinds. The surface area of each of the

\[\text{Fig. 1. Density distributions of a pure liquid in contact with three solid surfaces of different kinds (see text). a) Positive adsorption (concentration). b) Zero adsorption (isochoric conditions). c) Negative adsorption (dilatation). The shaded areas are equal to }\rho(z^\sigma - z^l) = \rho(z^\beta - z^l)\].