

CRITICAL EVALUATION OF THE LINEAR APPROXIMATION OF THE INDIVIDUAL ADSORPTION ISOTHERMS OF BINARY LIQUID MIXTURES ON SOLID SURFACES

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Introduction

A crucial point in the investigation of adsorption from liquid mixtures on solid surfaces is the determination of the true material content and composition of the interfacial phase, i.e. of the so-called individual isotherms $n_i^s = n_i^s(x_i)$ and $m_i^s = m_i^s(w_i)$. However, only the characteristics of the homogeneous solution phase can be measured directly, from which only the dependence of the specific mixture adsorption on the composition, i.e. the excess isotherm, can be determined without any assumptions, while the next step, leading to the determination of the individual isotherms, involves of necessity more or less arbitrary assumptions concerning the interfacial phase.¹

An important problem is the kind of relationship existing between the shape of the tested individual isotherms and the type of the "apparent" excess isotherm determined by them. The aim of our work was the critical evaluation of a possible linear approximation of the initial and final sections of the individual isotherms.

Since our investigations are extended besides the customary mole representation also to mass representation equivalent to the former, in addition to the explanation of concepts and symbols, also relationships of general validity between the two kinds of representations are presented.

The so-called reduced surface excess of the i -th component (in binary mixtures $i = 1, 2$) in the equilibrium system of an insoluble solid adsorbent of unit mass and a binary liquid mixture of a quantity $n = n_1 + n_2$ and a mass $m = m_1 + m_2$ is:

$$n_i^{\sigma} = n_i - nx_i = n(x_i^0 - x_i)$$

and

$$m_i^{\sigma} = m_i - mw_i = m(w_i^0 - w_i)$$

where $x_i(w_i)$ and $x_i^0(w_i^0)$ are molar fractions (mass fractions) of the i -th com-

ponent in the equilibrium bulk phase and in the liquid mixture before adsorption, respectively. By definition:

$$n_1^\sigma + n_2^\sigma = 0$$

and

$$m_1^\sigma + m_2^\sigma = 0. \quad (2)$$

The excess quantities (n_i^σ and m_i^σ) are independent of the total quantity of substances n and m , as long as these quantities are sufficient for the development of the inhomogeneous, adsorbed phase of quantity $n^s = n_1^s + n_2^s$ and $m^s = m_1^s + m_2^s$. From the general relationships

$$n_1^\sigma = n_1x_2 - n_2x_1$$

and

$$m_1^\sigma = m_1w_2 - m_2w_1 \quad (3)$$

and from Eqs (1), the excess is simple to express in terms of the material content of the interfacial phase²:

$$n_1^\sigma = n_1^s x_2 - n_2^s x_1$$

and

$$m_1^\sigma = m_1^s w_2 - m_2^s w_1. \quad (3a)$$

Eqs (3a) represent a direct functional relationship between the individual isotherms and the excess isotherm, therefore our aim is their discussion for the case of linear approximation of the individual isotherms in the dilute solution ranges.

On the basis of the relationship between mole fraction and mass fraction, the transformation of the two representations is

$$m_1^\sigma = n_1^\sigma (M_2 w_1 + M_1 w_2) \quad (4)$$

where M_1 and M_2 are the respective molecular weights. The two representations, though their formal identity exist only in the trivial case $M_1 = M_2$, are equivalent from the point of view of both the Schay—Nagy's isotherm classification and the adsorption capacity determination. On the basis of

$$\frac{dm_1^\sigma}{dw_1} = \frac{dn_1^\sigma}{dx_1} \frac{M_1 M_2}{M_2 w_1 + M_1 w_2} + n_1^\sigma (M_2 - M_1) \quad (5)$$

and

$$\frac{d^2 m_1^\sigma}{dw_1^2} = \frac{d^2 n_1^\sigma}{dx_1^2} \frac{M_1^2 M_2^2}{(M_2 w_1 + M_1 w_2)^3} \quad (6)$$

an eventual linear section, inflection or zero point of the excess isotherm are seen to belong to an identical composition in both representations. It should be mentioned that the separation factor α of the adsorption is not a function of the representation:

$$\alpha = \frac{x_1^s x_2}{x_2^s x_1} = \frac{w_1^s w_2}{w_1^s w_1} \quad (7)$$

Linear approximation of the $x_1 \ll 1$ sections of the individual isotherms

The linear approximation³ simulating the initial and final sections of the individual isotherms in the range $x_1 \ll 1$ is:

$$n_1^s = ax_1, \text{ where } a \geq 0 \quad (8)$$

and

$$n_2^s = \frac{1}{\beta} (n_{1,0}^s - ax_1) \quad (9)$$

under consideration of the so-called Williams' relationship representing the displacing and substituting character of liquid mixture adsorption:⁴

$$\frac{n_1^s}{n_{1,0}^s} + \frac{n_2^s}{n_{2,0}^s} = 1 \quad (10)$$

where $n_{i,0}^s$ is the adsorption capacity for the i -th pure component, and the substitution ratio determined by the molar space requirements is

$$\beta = \frac{n_{1,0}^s}{n_{2,0}^s} \quad (11)$$

The mass representations of linear individual isotherm equations (8) and (9)

$$m_1^s = aM_1M_2 \frac{w_1}{M_2w_1 + M_1w_2} \quad (8a)$$

and

$$m_2^s = \frac{1}{\beta} \frac{M_2}{M_1} \left[m_{1,0}^s - aM_1M_2 \frac{w_1}{M_2w_1 + M_1w_2} \right] \quad (9a)$$

are not linear with the exception of the trivial case $M_1 = M_2$, so that the two kinds of representation are not equivalent with respect to the individual isotherms. However, in view of the equivalence existing for the excesses, for example, the conclusions drawn for the excess isotherm from the individual isotherms approximated in mole representation by a linear relationship, are valid without any modifications also for the mass excess, in spite of the fact that the mass representation of the individual isotherms cannot be linearly approximated. Therefore, in the following only the mole representation will be discussed in detail.

According to the linear combination of the individual isotherms (3a) approximated by linear equations (8) and (9), in the range of validity of approximation ($x_1 \ll 1$) the excess isotherm is:

$$n_1^\sigma = \frac{1}{\beta} (a - n_{1,0}^s) x_1 + \frac{\beta - 1}{\beta} a x_1 x_2 \quad (12)$$

and the separation factor

$$\alpha = \frac{a x_2 \beta}{n_{1,0}^s - a x_1} \quad (13)$$

Thus the shape of the excess isotherm and the magnitude of the separation factor are determined by the slope a of the individual isotherms and by the ratio of the space requirement of the components β . The first derivative gives information on the sign of the excess isotherm to start from the origo, while the second derivative gives information on the direction of the curvature. From (12):

$$\left(\frac{dn_1^\sigma}{dx_1} \right)_{x_1=0} = a - \frac{n_{1,0}^s}{\beta} \quad (14)$$

and

$$\left(\frac{d^2 n_1^\sigma}{dx_1^2} \right)_{x_1=0} = 2a \frac{1 - \beta}{\beta}, \quad (15)$$

and, from Eq.(13), the extreme value of the separation factor at $x_1 = 0$ is

$$(\alpha)_{x_1=0} = \frac{a\beta}{n_{1,0}^s} \quad (16)$$

while, on the basis of Eq. (7), $\alpha > 1$ means the positive adsorption of component 1.

Let us group the individual isotherms on the basis of the slope of the initial linear section in the following way: the individual isotherm is considered as of positive deviation in the said initial section if $a > n_{1,0}^s$, i.e. if the individual $n_1^s = a x_1$ isotherm lies above the linear individual isotherm $n_1^s = n_{1,0}^s x_1$, which can be formally written for the total composition range, while in the opposite case it is considered as of negative deviation. Whether the concentration of a certain component increases or decreases at the interface, i.e. whether positive or negative adsorption corresponds to a deviation of given sign interpreted in this way, is determined by the relative space requirement of the components.

If the individual isotherm of component 1 is of extreme negative deviation along the initial linear section $x_1 \ll 1$, i.e. in the limit case $a = 0$:

$$\begin{aligned}
 n_1^s &= 0 \\
 n_2^s &= \frac{n_{1,0}^s}{\beta} = n_{2,0}^s \\
 n_1^\sigma &= -n_{2,0}^s x_1 \\
 \alpha &= 0.
 \end{aligned}$$

Thus, the interfacial phase is formed by the pure component 2, the excess isotherm is of type II, and evidently, independently of the β ratio of space requirements, the adsorption of the component with positive deviation (in the present case of subscript 2) will be positive (Fig. 1).

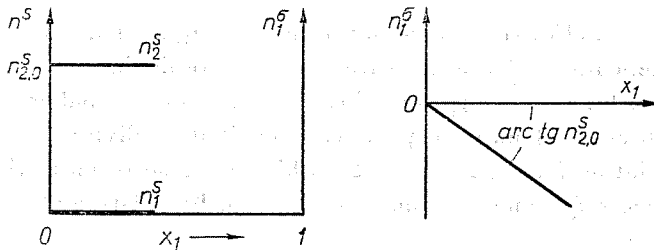


Fig. 1. Individual isotherms and excess isotherm in the range $x_1 \leq 1$ in the case of linear approximation with extreme ($a = 0$) deviation

In the general case, the linear section of the individual isotherms is of finite deviation ($a \neq 0$). To consider these cases, the range $x_1 \ll 1$ discussed above in detail, as well as the range $x_2 \ll 1$ close to the other pure component, will be investigated separately. Our discussion will be reduced to the case $\beta > 1$, i.e. where the space requirement of component 1 is the smaller. In view of the fact that on exchanging the subscripts $\beta < 1$ would be obtained, mutatis mutandis, the conclusions can be applied to the excess isotherm of the component of larger space requirement.

On the basis of Eqs (12 to 16), for a general deviation $a > 0$ of the linear individual isotherm and $\beta > 1$, the following cases may arise in the range $x_1 \leq 1$ (see Fig. 2):

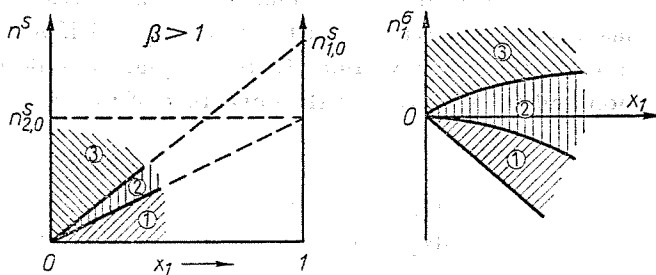


Fig. 2. Individual isotherms and excess isotherms in the range $x_1 \leq 1$ in the case of linear approximation with any ($a \geq 0$) deviation, ($\beta > 1$)

Measure of deviation	Deviation of n_1^s	Sign of n_1^{σ}
1. $0 \leq a \leq \frac{1}{\beta} n_{1,0}^s$	-	-
2. $\frac{1}{\beta} n_{1,0}^s < a < n_{1,0}^s$	-	+*
3. $n_{1,0}^s < a$	+	+

* but it can change sign in the immediate vicinity of $x_1 = 0$

According to Eq. (15), the excess isotherm $n_1^{\sigma} = n_1^{\sigma}(x_1)$ is in all the above cases concave, independent of the measure of the finite deviations.

Apparently, the adsorption of the component of smaller space requirement (of subscript 1) may be positive even if its individual isotherm has a negative deviation (range 2 in Fig. 2), while the adsorption of the component of larger space requirement (component 2) can be positive at a high positive deviation only.

For the final section ($x_2 \ll 1$) of the individual isotherm $n_1^s = n_1^s(x_1)$, the linear approximation and the expressions following from it, by analogy to the range $x_1 \ll 1$, are:

$$n_1^s = n_{1,0}^s - bx_2 \text{ where } b \geq 0 \quad (8b)$$

$$n_2^s = \frac{1}{\beta} bx_2 \quad (9a)$$

$$n_1^{\sigma} = (n_{1,0}^s - b)x_2 + \frac{\beta - 1}{\beta} bx_1 x_2 \quad (12a)$$

$$\alpha = \beta \frac{n_{1,0}^s - bx_2}{bx_1} \quad (13a)$$

In accordance with the earlier interpretation, the linear individual isotherm of component 1 has a positive deviation in the range $x_2 \ll 1$ if $b < n_{1,0}^s$, and in the opposite case, a negative deviation. Critical quantities determining the sign of adsorption and the direction of the curvature of the excess isotherm at $x_1 = 1$ are:

$$\left(\frac{dn_1^{\sigma}}{dx_1} \right)_{x_1=1} = \frac{b}{\beta} - n_{1,0}^s \quad (14a)$$

$$\left(\frac{d^2 n_1^{\sigma}}{dx_1^2} \right)_{x_1=1} = 2b \frac{1 - \beta}{\beta} \quad (15a)$$

$$(\alpha)_{x_1=1} = \beta \frac{n_{1,0}^s}{b} \tag{16a}$$

on the basis of Eqs (12a to 16a), for a general deviation $b > 0$ of the linear individual isotherms, and $\beta > 1$, cases likely to occur in range $x_2 \ll 1$ (see Fig. 3):

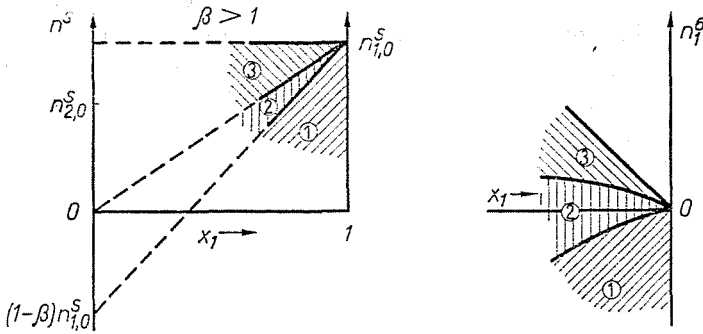


Fig. 3. Individual isotherms and excess isotherms in the range $x_2 \ll 1$ in the case of linear approximation with any ($b \geq 0$) deviation, ($\beta > 1$)

Measure of deviation	Deviation of n_1^s	Sign of n_1^σ
1. $\beta n_{1,0}^s \leq b$	-	-
2. $n_{1,0}^s < b < \beta n_{1,0}^s$	-	+*
3. $0 \leq b < n_{1,0}^s$	+	+

* but it can change sign in the immediate vicinity of $x_1 = 1$

According to Eq. (15a), the excess isotherm $n_1^\sigma = n_1^\sigma(x_1)$ is concave also in the range $x_2 \ll 1$ in the case $\beta > 1$, independent of the measure of the finite deviation.

The relationship between the deviation of the individual isotherm of linear approximation and the sign of adsorption in the range $x_2 \ll 1$, is identical with that found for case $x_1 \ll 1$, i.e. the adsorption of the component with larger space requirement can be positive in the case only, when the positive deviation of the individual isotherm is high, whereas the component with smaller space requirement can be enriched at the surface even in the case of its small negative deviation.

Conclusions

The composition-dependence of the true material content in the interfacial phase, developing at the surface of the solid adsorbent in adsorption from binary liquid mixtures, the individual isotherm $n_i^s = n_i^s(x_i)$ has been determined by linear approximation in the initial and final concentration ranges $x_i \ll 1$. The direction of the curvature of the excess isotherm, resulting from the combination of individual isotherms approximated linearly in finite length at both ends of the total composition range, was found to be identical in both dilute solution ranges, because it depended exclusively on the ratio of the space requirement of the components, supposed having no concentration dependence in physical adsorption. Thus, when linear approximation is valid, the excess isotherm of the component with smaller space requirement is concave along both its initial and final section, while that of the component with larger space requirement is convex. Evidently, with this mode of discussion excess isotherms with one inflection (types III, IV and V) cannot be simulated, the applicability of the method for both ends of the composition range is thus restricted to the description of positive adsorption of type I or II of the component with smaller space requirement.

Summary

The aim of the work was to find a relationship between the excess adsorption isotherm accessible to experiments without any assumptions and characteristic of the adsorption of binary liquid mixtures on solid surfaces, as well as the experimentally inaccessible individual adsorption isotherms, representing the amount and composition of the interfacial phase. The individual isotherms were assumed to be accessible to linear approximation over a finite length in the ranges of dilute solution. In this case, the direction of the curvature of the excess isotherm is determined exclusively by the relative space requirement of the components. Therefore, a linear approximation of the individual isotherms is justified only in the description of the positive adsorption of type I or II of the component with smaller space requirement.

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