

Focusing Review

Concept of Surface Excess Amount and Applications for Native and Modified Surfaces

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Abstract

For surface excess amount and calculating it from chromatographic retention data, some important equations were summarized and the approximations involved were described. Then the layer model was introduced and used to calculate the composition of the adsorbed phase and estimate the absolute adsorbed amount. The surface properties of unmodified and chemically modified silica were characterized by measuring their surface excess isotherm.

Keyword: surface excess amount, solvent disturbance peak, retention volume of the labeled components, the layer model

1. Introduction

The popularity of reversed phase separations, particularly with C₁₈ bonded packing materials, could be attributed to the success of this technique in solving a diverse array of problems. The question of why it makes mixture separate might have given some chromatographers mission and passion of elucidating retention mechanism. The difficulty in describing the retention process in reversed phase liquid chromatography (RPLC) comes from the difficulty to know nature of the bonded phase itself. The question of whether a bonded phase should be considered a surface or a thin liquid film has given to raise two theories of solute retention in RPLC: adsorption and partition. Adsorption means the interaction of the stationary phase with the solute or solvent molecules covering the external molecular layer of the adsorbent. In the simplest case, adsorption is characterized by a monolayer in which the solute and solvent molecules are in competition to cover the external surface of the packing material. In a partition process, sole role of the stationary phase is to create a large surface area where the stationary liquid phase will be deposited. The phenomena in the interfacial region are then generally neglected and the solute molecules are partitioned into the two liquid phases. Each phase contains two com-

ponents: the solvent and solute in the mobile phase and the stationary liquid and solute in the stationary phase. Considerable effort has been paid by workers trying to classify retention as one of the two categories, but evidence for such a classification remains inconclusive. However, there is much evidence that the solvation of the bonded alkyl chains themselves changes in response to varying composition of the mobile phase. It is important for the chromatographers to know surface state of packing materials and this paper will or might give them helpful information.

In this paper, concept of surface excess amount was introduced and method of determining it from chromatographic retention data was practically described. On its application, attempt to characterize the surface properties of unmodified and chemically modified silica by measuring their surface excess isotherm was made by using four kinds of silica.

2. Concept of Surface Excess Amount

Quantitative definitions for the adsorption of binary liquid mixture at solid-liquid interfaces in terms of surface excess amounts were given by Everett [1]. Riedo and Kováts [2] derived general relationships for calculating these surface excess amounts

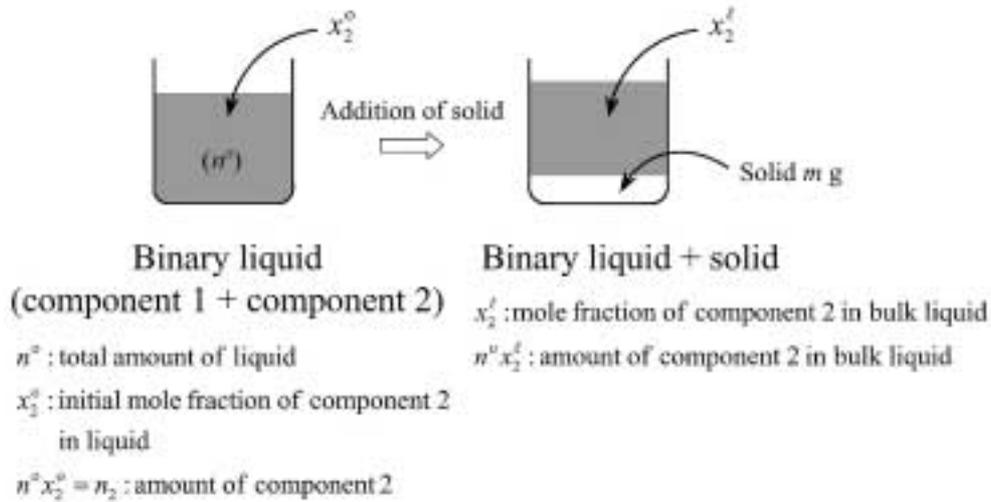


Figure 1. The explanation of surface excess amount (amount of adsorption) by means of a picture

from chromatographic retention data. Here some important equations are summarized and the approximations involved are described.

A sample of a binary liquid mixture containing an amount n^o at a mole fraction x_2^o is equilibrated with a mass m of solid. The final mole fraction x_2^l is experimentally determined after the solid adsorbs component 1 or 2 and it comes to stable equilibrium. The explanation of surface excess amount (amount of adsorption) by means of a picture is shown in Figure 1. The reduced surface excess of component 2, $n_2^{\sigma(n)}$, is then given by the equation

$$n_2^{\sigma(n)} = n^o x_2^o - n^o x_2^l = n_2 - n^o x_2^l \quad (1)$$

where n_2 is amount of component 2. The areal reduced surface excess,

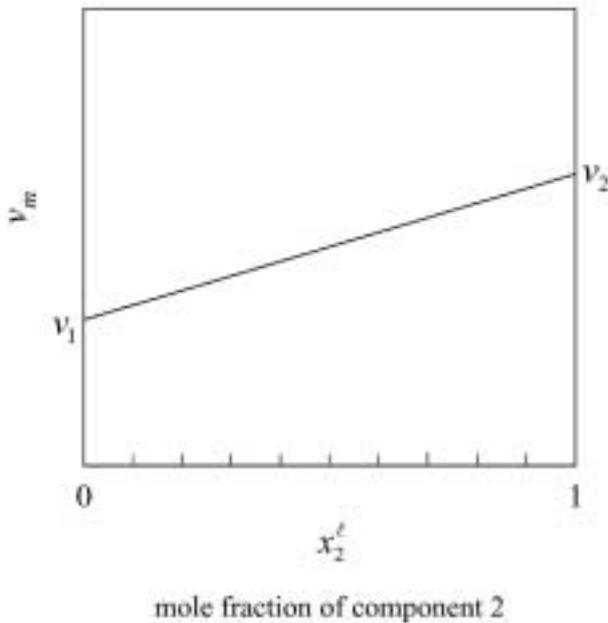


Figure 2. Mean molar volume plotted as a linear function of x_2^l in binary liquid

denoted by $\Gamma_2^{(n)}$, is defined as

$$\Gamma_2^{(n)} = n_2^{\sigma(n)} / mS \quad (2)$$

where S is the specific surface area of the solid. If adsorption from solution is represented in terms of liquid volumes and volume concentrations, equation 1 should be described as equation 3 where $n_2^{\sigma(v)}$ is reduced surface excess of component 2 on volume basis, V^o ($= n_1 v_1 + n_2 v_2$, where v_1 and v_2 are the partial molar volume of components 1 and 2) is the initial volume of liquid, and c_2^l is the concentration of component 2 in bulk liquid.

$$n_2^{\sigma(v)} = n_2 - V^o c_2^l \quad (3)$$

If it assumes that the mean molar volume of the liquid mixture, v_m ($v_1 x_1^l + v_2 x_2^l$, where x_1^l and x_2^l are the mole fraction of components 1 and 2), is a strictly linear function of the mole fractions as shown in figure 2 (i.e., when the partial molar volumes, v_1 and v_2 , of the components are constant over the concentration range considered), the following relationship will be obtained.

$$n_2^{\sigma(v)} = [1 + (v_1 - v_2) c_2^l] n_2^{\sigma(n)} = \frac{v_1}{v_m} n_2^{\sigma(n)} \quad (4)$$

3. Determination of Surface Excess Amount by Chromatographic Method

3.1. Method for determining surface excess amount by the retention volume of the solvent disturbance peak

Let us consider a liquid solution flowing through a packed column with a uniform cross-section area. The equation of material balance for component 2 in the section from the column inlet to distance z can be written as follows, assuming one-dimensional plug flow under being absence of longitudinal diffusion:

$$(1/L) \frac{\partial n_2}{\partial t} = -F \frac{\partial c_2^l}{\partial z} \quad (5)$$

where L is the column length and F represents the flow rate, which is presumed to be constant throughout the column. Substituting equation 3 into equation 5 gives the material balance in terms of surface excess amount.

$$\frac{\partial}{\partial t} (n_2^{\sigma(v)} + V^o c_2^\ell) = -FL \frac{\partial c_2^\ell}{\partial z} \quad (6)$$

For a binary liquid, the surface excess isotherm is a function of the concentration c_2^ℓ . Hence, the transport equation becomes

$$(V^o + dn_2^{\sigma(v)} / dc_2^\ell) \frac{\partial c_2^\ell}{\partial t} = -FL \frac{\partial c_2^\ell}{\partial z} \quad (7)$$

Equation 7 can be solved for the case when the sample enters the column in a very short time, resulting in an equation for the migration velocity u_x of a concentration c_2^ℓ .

$$\frac{\partial z}{\partial t} = u_x = FL / (V^o + dn_2^{\sigma(v)} / dc_2^\ell) \quad (8)$$

From equation 8, an expression which described the residence time t_R of the concentration c_2^ℓ in the column can be derived.

$$t_R = L / u_x = (V^o + dn_2^{\sigma(v)} / dc_2^\ell) / F \quad (9)$$

$$F t_R = V_R = V^o + dn_2^{\sigma(v)} / dc_2^\ell$$

By the approximation of $V^o \approx V_m$, the retention volume of the solvent disturbance peak, V_R provides the first derivative of the surface excess isotherm,

$$dn_2^{\sigma(v)} / dc_2^\ell = V_R - V_m \quad (10)$$

where V_m is the column hold-up volume. In this case components 1 and 2 correspond to water and organic modifier, respectively. Experimental points $(V_R - V_m)$ determined at given composition of the

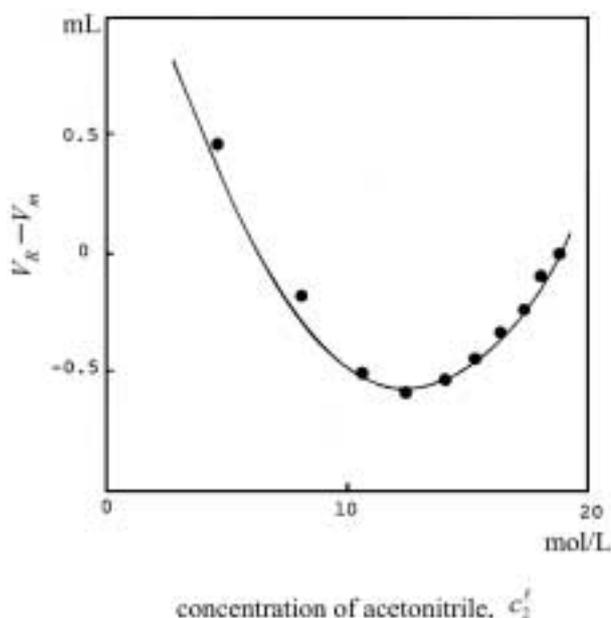


Figure 3. An example of the experimental points $(V_R - V_m)$ and the regression curve with monomeric C_{18} phase Eluent: water-acetonitrile

eluent plotted as a function of c_2^ℓ show parabolic curves. Therefore, the quadratic expression is fitted on the experimental points. In Figure 3 for example the regression curve is compared with the experimental points. The areal reduced surface excess of component 2, $\Gamma_2^{(n)}$, is given by equation 2 when $n_2^{\sigma(v)}$ is calculated by the integration of the equation 10 and converted to $n_2^{\sigma(n)}$ by equation 4.

3.2. Method for determining surface excess amount by the retention volume of the labeled components

The separation surface is resulted from an arbitrary choice and is generally in a position such that the Gibbs' surface excess for the solvent is zero. Therefore, the areal reduced surface excess of component 1, $\Gamma_1^{(n)}$, is

$$\Gamma_1^{(n)} = -\Gamma_2^{(n)} \quad (11)$$

In the case of using the retention volume of the labeled components, 1* and 2*, in the eluent instead of the perturbation of the concentration c_2^ℓ , the areal reduced surface excess, $\Gamma_2^{(n)}$, is given by the combination of the results with equation 11.

$$\Gamma_2^{(n)} = (V_{R,2^*} - V_{R,1^*}) x_2^\ell x_1^\ell / mSv_m \quad (12)$$

where V_R is the retention volume, m and S are the mass and specific surface area of column packing.

4. The layer model

In the case of dealing with an actual system, it is not enough to get the surface excess isotherm, because it only represents the total change of the system and does not refer to the actual quantity of a component present in the mobile phase and in the adsorbed phase. Therefore, the layer model [1] was used to calculate the composition of the adsorbed phase and estimate the absolute adsorbed amount.

Assuming that the adsorbed phase consists of t layers of molecules on a smooth, planar homogeneous surface, the mole fraction, x_2^s , of component 2 in the surface phase is given by

$$x_2^s = \frac{t x_2^\ell + a_1^o \Gamma_2^{(n)}}{t - (a_2^o - a_1^o) \Gamma_2^{(n)}} \quad (13)$$

where a_1^o and a_2^o are the molar cross-sectional areas of components 1 and 2, which can be calculated from the partial molar volume, v_1 and v_2 , with the equation $a_i^o = 9200 (v_i)^{2/3}$ ($i = 1, 2$). This equation is based on the assumption that a molecule is a rigid sphere and has a face-centered cubic structure. Assuming this, $a_i^o = 2\sqrt{3}r^2 N$ and $r = (v_i / 4\sqrt{2} N)^{1/3}$ are obtained, where r is a molecular radius and $N = 6.0 \times 10^{23}$. Using these a_i^o values, and the experimental surface excess data, $\Gamma_2^{(n)}$, the minimum number of layers, t_{\min} , is estimated by satisfying the criteria that values of x_2^s calculated do not exceed unity, and x_2^s always increases with x_2^ℓ (i.e., $(\partial x_2^s / \partial x_2^\ell) > 0$). There-

Table 1. Characteristics of the adsorbents

	surface area (m ² /g)	% carbon	surface coverage (μmol/m ²)	mean pore diameter (nm)
A-300	67	–	–	38.2
A-C ₁₈	50	4.9	3.25	35.2
B-300	168	–	–	27.4
B-C ₁₈	123	10.2	2.91	26.0
C-300	82	–	–	39.8
C-C ₁₈	70	5.5	3.03	37.6
D-300	107	–	–	35.2
D-C ₁₈	82	6.7	2.85	32.8

fore, x_2^s is calculated by equation 13 with values of t_{\min} .

5. Application

The attempts to characterize the surface properties of unmodified and chemically modified silica by measuring their surface excess isotherm. Four kinds of silica (A-300, B-300, C-300 and D-300 purchased from A, B, C and D manufacturers) were used as native surfaces and then were chemically modified by using the conventional preparation method of the monomeric C₁₈ phase. Details about the characteristics of the column packing are summarized in Table 1. The chromatographic method to determine the surface excess isotherms was based on measurements of the retention volumes of labeled components of the eluent constituents.

5.1. Procedures

The column materials were packed by means of a balanced slurry technique into 250 x 4.6 mm i.d. stainless steel tubes. The column hold-up volume was determined by injecting small pulses of deuterated acetonitrile in pure acetonitrile mobile phase. The retention volume was obtained from the flow rate that was measured by the volumetric flask method and retention time. The sample concentration was chosen as low as possible while maintaining suitable single-to-noise ratio in RI detection. Eluents of appropriate compositions were prepared by weighing.

5.2. Results and Discussion

To observe the changes on the surface of unmodified and chemically modified silica, the surface excess isotherm were determined in aqueous acetonitrile at 30°C. In Figures 4 and 5, the areal reduced surface excess amount are plotted against the mole fraction, x_2^s . A-C₁₈, as well as A-300, adsorbed a large quantity of water as seen in Figure 4. This result suggested that A-C₁₈ had still a great number of silanol groups regardless of relatively high coverage. On the other hand, the other modified surfaces selectively adsorbed acetonitrile as can be seen in Figure 5. This meant that

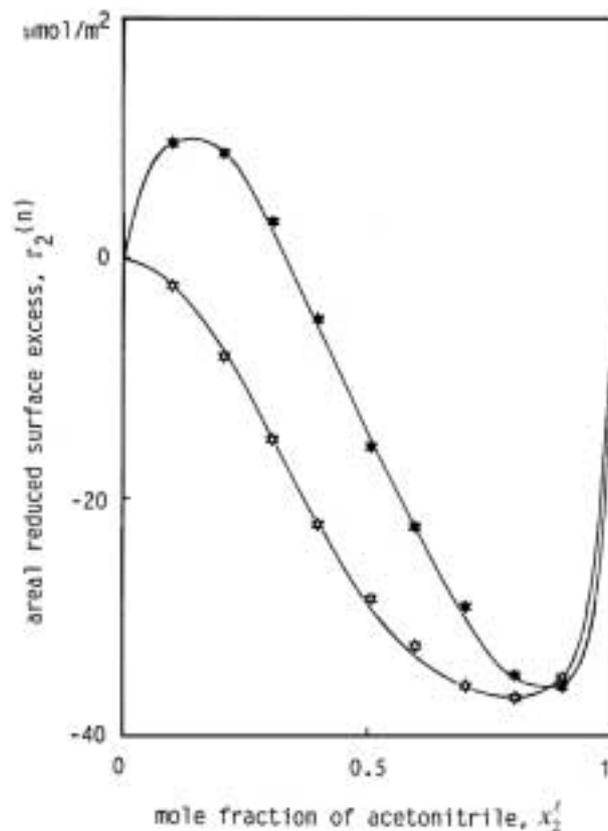


Figure 4. The surface excess amount of acetonitrile adsorbed at 30 °C from an aqueous mixture onto (○) A-300 and (★) A-C₁₈ plotted against the mole fraction of acetonitrile.

the silica surface, which had a strong affinity for water, was mostly covered with alkyl chains that had hydrophobic property. In order to determine the actual quantity of a component present in the adsorbed phase on the surface, the minimum number of layers, t_{\min} , and the mole fraction of the adsorbed phase, x_2^s , were calculated by using the layer model. These results are shown in Table 2 and Figure 6. The modified surface should be greatly depended upon the native one in the concern of the surface excess amount because the surface excess amount of the modified surface was predicted to be the sum of those of the alkyl chains and the native one.

Silanol groups on the surface are commonly known to be either isolated or hydrogen bonded. The majority is weakly acidic although a small proportion is strong acidic and is ionized even at low pH. It is popularly reported that the small portion of silanol groups causes undesired adsorption of basic compounds. To determine the change of the highly acidic silanol groups before and after the modification of silica, the retention of pyridine was measured with acidic aqueous acetonitrile mobile phase. A-300 and A-C₁₈ did not retain protonated pyridine. It is speculated that A-300 had a great number of ordinary silanol groups which were undissociated at pH below 3, and probably “buried” silanol groups [3].

In conclusion, the changes of surface excess isotherms before

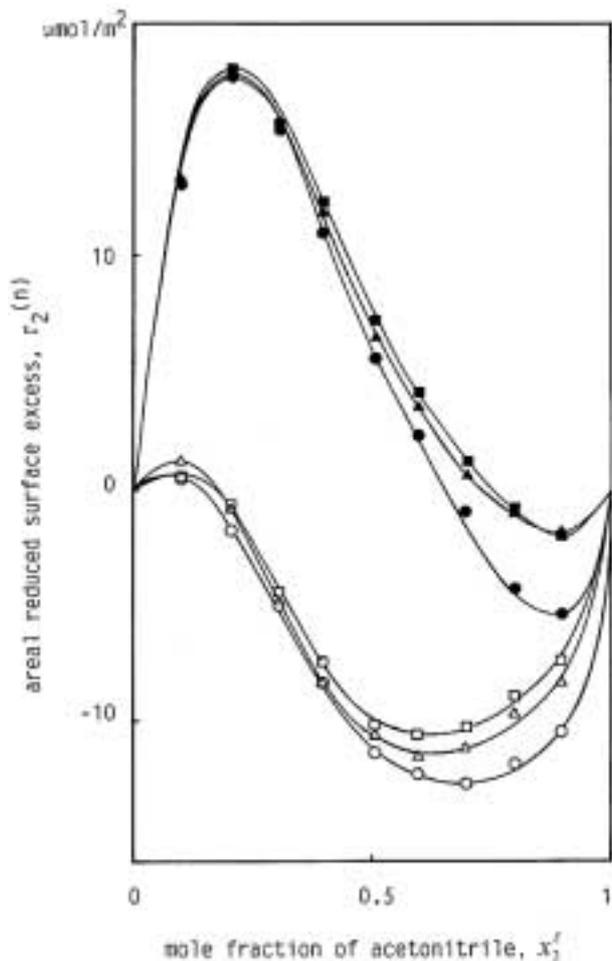


Figure 5. The surface excess amount of acetonitrile adsorbed at 30 °C from an aqueous mixture onto (○) B-300, (●) B-C₁₈, (△) C-300, (▲) C-C₁₈, (□) D-300 and (■) D-C₁₈ plotted against the mole fraction of acetonitrile.

Table 2. The values of t_{min} satisfied the criteria

	A-300	A-C ₁₈	B-300	B-C ₁₈	C-300	C-C ₁₈	D-300	D-C ₁₈
t_{min}	6	9	3	6	4	6	3	5

and after the modification of silica reflected turning from hydrophilic surface into hydrophobic ones. A-300 was found to have a great number of buried silanol groups.

List of Symbols

- a_i^o molar cross-sectional areas of component i, cm²/mol
- c_2^o concentration of component 2 in bulk liquid, mol/L
- F flow rate, mL/min
- L column length, cm
- m mass of solid, g
- N Avogadro constant, mol⁻¹
- n^o total amount of liquid, mol

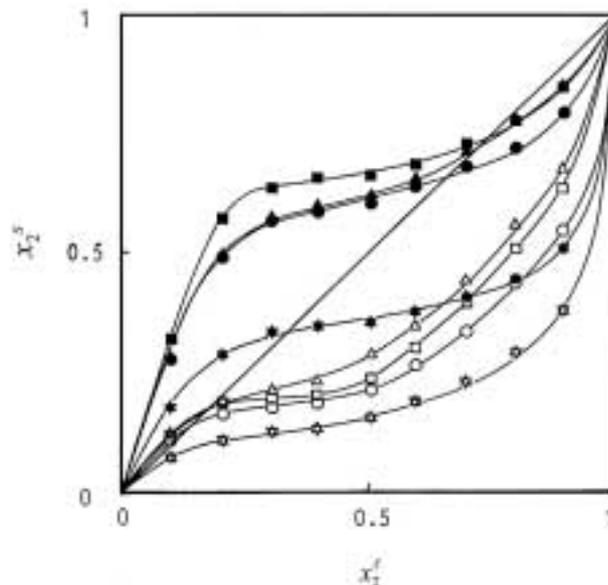


Figure 6. The composition of the adsorbed phase at 30 °C from an aqueous mixture onto (☆) A-300 and (★) A-C₁₈, (○) B-300, (●) B-C₁₈, (△) C-300, (▲) C-C₁₈, (□) D-300 and (■) D-C₁₈ plotted against the mole fraction of acetonitrile.

- n_i amount of component i, mol
- $n_2^{σ(n)}$ reduced surface excess of component 2, mol
- $n_2^{σ(v)}$ reduced surface excess of component 2 on volume basis, mol
- r molecular radius, cm
- S specific surface area, m²/g
- t thickness of adsorbed layer
- t_{min} minimum number of layers
- t_R residence time = retention time, min
- u_x migration velocity of sample, cm/min
- V^o initial volume of liquid, mL
- V_m column hold-up volume, mL
- V_R retention volume, mL
- v_m mean molar volume of the liquid mixture, mL/mol
- v_i partial molar volume of component i, mL/mol
- x_2^o initial mole fraction of component 2 in liquid
- x_i^o mole fraction of component i in bulk liquid
- x_2^s mole fraction of component 2 in surface phase
- z distance from column inlet, cm
- $Γ_i^{(n)}$ areal reduced surface excess of component i, μmol/m²

References

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