Use of lipophilic ion adsorption isotherms to determine the surface area and the monolayer capacity of a chromatographic packing, as well as the thermodynamic equilibrium constant for its adsorption

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Abstract

A method that champions the approaches of two independent research groups, to quantitate the chromatographic stationary phase surface available for lipophilic ion adsorption, is presented. For the first time the non-approximated expression of the electrostatically modified Langmuir adsorption isotherm was used. The non approximated Gouy–Chapman (G–C) theory equation was used to give the rigorous surface potential. The method helps model makers, interested in ionic interactions, determine whether the potential modified Langmuir isotherm can be linearized, and, accordingly, whether simplified retention equations can be properly used. The theory cultivated here allows the estimates not only of the chromatographically accessible surface area, but also of the thermodynamic equilibrium constant for the adsorption of the amphiphile, the standard free energy of its adsorption, and the monolayer capacity of the packing. In addition, it establishes the limit between a theoretical and an empirical use of the Freundlich isotherm to determine the surface area. Estimates of the parameters characterising the chromatographic system are reliable from the physical point of view, and this greatly validates the present comprehensive approach.
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1. Introduction

The estimation of physicochemical properties by chromatographic techniques is a very important topic. A special volume of *Journal of Chromatography A*, vol. 1037, was dedicated to this question. The determination of the surface area of chromatographic packings is usually performed via the BET method using N_2 as a probe adsorbate. Obviously the surface accessibility for irregular materials depends on the size of the probe molecule: if it is large it is not able to follow the irregularity of the surface [1]. Lipophilic ions (H) are typical ion interaction reagent (IIR) used in ion interaction chromatography (IIC) [2–6], also referred to as ion-pair chromatography [7–11]. Their adsorption from aqueous solutions onto reversed phase materials has been presented by Hagglund and Stahlberg [12] as an attractive method for the determination of the chromatographically accessible area of the chromatographic packing (octadecyl-bonded silica). Those authors used a linearized potential modified Langmuir adsorption isotherm; the surface potential (Ψ°) due to the lipophilic ion adsorption was defined with a solution of the linearized Poisson–Boltzmann equation in cylindrical coordinates. Their approach is theoretically valid only (i) for a surface potential below 25 mM [13] otherwise the linear relationship between the surface potential and the surface concentration of the adsorbed H ions does not hold anymore, and (ii) if the linearization of the isotherm is feasible. Unfortunately, both conditions are seldom encountered in the chromatographic practice that involves the use of large, amphiphilic ions to

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enlarge retention of ionized samples: the increase in the concentration of H even up to values just below the critical micelle concentration is a typical optimization procedure in IIC [2–11]. In the chromatographically meaningful concentration range of the amphiphile, the linearized form of the isotherm is easily predicted not to hold. A modified version of the theory was recently forward by Niederhauser et al. [14] and applied to a column containing a polystyrene-divinylbenzene resin. As in the approach by Hagglund and Stahlberg, the linearized potential modified Langmuir isotherm was selected to describe adsorption data, but Ψ° was given as a function of the adsorbed amphiphile by the Gouy–Chapman (G–C) theory equation under the hypothesis of a semi-infinite geometry. The latter assumption is only valid at high ionic strength. We will demonstrate that their description, and particularly the linearization of the isotherm, is not acceptable for the data set under study. This is probably the reason for some lack of fit of experimental results. The present paper seeks to expand upon the earlier work and to examine the limits of applicability of a number of approximations. The integral form of the electrostatically modified Langmuir adsorption isotherm was used for the first time, since we demonstrate that its linearization is not usually acceptable under typical experimental conditions in IIC, as already observed [7,10].

2. Theory

For a lipophilic ion H, the Langmuir isotherm does not hold because the electrostatic surface potential, due to the stronger retention of H compared to its counterion, runs counter to its further adsorption, and hence surface coverage is less than that predicted in the absence of the surface potential. If one takes into account that at equilibrium the rate of adsorption and desorption should be identical, an electrostatically modified Langmuir adsorption isotherm can be obtained [15]. For H the potential modified Langmuir adsorption isotherm can also be easily obtained from the thermodynamic equilibrium constant (K_{LH}) for its adsorption onto the stationary phase free ligand site (L):

$$L + H \xrightarrow{K_{LH}} LH \tag{1}$$

If the counter ion of H is not strongly adsorbophilic, it was demonstrated to be [2]:

$$K_{LH} = \frac{a_{LH}}{a_L a_H} \exp\left(\frac{z_H F \Psi^{\circ}}{RT}\right) \tag{2}$$

where a is the activity coefficient for each species, z_H is the charge of the IIR, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. In Eq. (2) the ratio of the activity coefficients can be considered a constant. This approximation is usually acceptable in the chromatographic practice of IIC, since ionic strength is kept constant

by the use of a compensatory electrolyte to avoid spurious effects on the surface potential and salting-in or salting-out [2–8,10,11]. For similar reasons, the ionic strength was kept constant also in the experimental set-up for the determination of the chromatographically accessible surface area via the amphiphile adsorption in refs. [12,14]. It follows that we can write:

$$K_{LH} = \frac{[LH]}{[L][H]} \exp\left(\frac{z_H F \Psi^{\circ}}{RT}\right) \tag{3}$$

where [L] is the surface concentration of the free ligand sites and [LH] is the surface concentration of H, and [H] is its eluent concentration.

If $[L]_T$ is the total ligand sites concentration, that is the monolayer capacity ($\mu mol/m^2$) of the column, it can be written [2]:

$$[L]_T = [L] + [LH] \tag{4}$$

From Eqs. (3) and (4), the following potential modified Langmuir adsorption isotherm can be readily obtained:

$$[LH] = \frac{K_{LH}[L]_T[H] \exp(-z_H F \Psi^{\circ}/RT)}{(1 + K_{LH}[H] \exp(-z_H F \Psi^{\circ}/RT))} \tag{5}$$

This equation is usually linearized under the assumption that, as [H] approaches zero, the denominator approaches one. Actually this approximation does not hold for lipophilic IIRs, since the stationary phase coverage can be high even at very low eluent concentrations (see below) [7,10].

Moreover, in IIC the amphiphile concentration does not obviously approach zero, since it is advantageously added to the eluent to increase analytes retention. It follows that the adsorption isotherm should be recorded in a very wide concentration range to cover both surface area determination (very low concentrations) and retention prediction in IIC (medium-high concentrations).

For these reasons, that will be quantitatively confirmed by our results, we decided, for the first time, not to use the linearized form of this isotherm but the non approximated expression. Eq. (5) is not very useful for a practical test of the theory since [LH] depends on both [H] and Ψ°, but Ψ° itself depends on [LH] (see below). Its linearization [12,14] paved the way to a quite simple, but not very accurate, final relationship. From Eqs. (3) and (4), the following expression may be alternatively obtained:

$$[H] = \frac{[LH]}{K_{LH}([L]_T - [LH])} \exp\left(\frac{z_H F \Psi^{\circ}}{RT}\right) \tag{6}$$

Eq. (6) merits consideration. Even if it is algebraically equivalent to Eq. (5), it is more convenient to use because it allows one to obtain a simple expression without the linearization of the isotherm, as shown in the following.

The G–C solution for a semi-infinite geometry gives the surface potential as a function of [LH] [2,10]:

$$\Psi^\circ = \frac{2RT}{\mathrm{F}}\ln\left\{\frac{[\mathrm{LH}]|z_\mathrm{H}|F}{\left(8\varepsilon_0\varepsilon_\mathrm{r}RT\sum_i c_{0i}\right)^{1/2}}\right.$$
$$\left.+\left[\frac{([\mathrm{LH}]|z_\mathrm{H}|F)^2}{\left(8\varepsilon_0\varepsilon_\mathrm{r}RT\sum_i c_{0i}\right)^{1/2}}+1\right]^{1/2}\right\} \quad (7)$$

where ε is the dielectric constant of the medium, ε_0 is the vacuum permittivity, and $\sum_i c_{0i}$ is the mobile phase concentration of singly charged electrolytes. It is convenient to indicate:

$$f = \frac{|z_\mathrm{H}|F}{\left(8\varepsilon_0\varepsilon_\mathrm{r}RT\sum_i c_{0i}\right)^{1/2}} \quad (8)$$

where f is a constant which can be evaluated from experimental conditions. Eq. (7) corresponds to Eq. (7) of ref. [14], since $\sinh^{-1} x = \ln[x + (x^2 + 1)^{0.5}]$. According to Weber [16] the semi-infinite system does not properly apply if the pore size is of the same order of magnitude as the Debye length [16]. We find this geometry an acceptable approximation, since the pore diameter of most RPLC stationary phases usually ranges from 60 to 300 Å and in a typical IIC chromatographic set-up the mobile phase is buffered to control analyte ionization. Hence, the ionic strength of the eluent is usually such that the Debye length is one order of magnitude lower than the porous space dimension [2–11]. If we insert Eqs. (7) and (8) into Eq. (6) we have:

$$[\mathrm{H}] = \frac{[\mathrm{LH}]}{K_\mathrm{LH}([\mathrm{L}]_\mathrm{T} - [\mathrm{LH}])}([\mathrm{LH}]f + (([\mathrm{LH}]f)^2 + 1)^{0.5})^{2|z_\mathrm{H}|} \quad (9)$$

As anticipated above, Eq. (6) is attractive because, if we express Ψ° as a function of [LH] via Eq. (7), we have that [H] depends only on [LH] and the linearization of the isotherm may be avoided; nevertheless, the obtained Eq. (9) is very simple. This way, we may abstain from the trade-off between simplicity and accuracy: this is the crucial improvement of the present development of the theory.

In this expression we have only two variables: K_LH and $[\mathrm{L}]_\mathrm{T}$. Actually, if the chromatographic area of the packing is unknown we may express [LH] as LH/A, where LH represents the total micromoles of IIR adsorbed onto the stationary phase, A is the chromatographically accessible surface area, and $[\mathrm{L}]_\mathrm{T}$ as L_T/A where L_T indicates the total free ligand sites (monolayer capacity, μmol). We obtain the following expression that will be used to test the present theory:

$$[\mathrm{H}] = \frac{\mathrm{LH}}{K_\mathrm{LH}(L_\mathrm{T} - \mathrm{LH})}\left(\frac{\mathrm{LH}f}{A} + \left(\left(\frac{\mathrm{LH}f}{A}\right)^2 + 1\right)^{0.5}\right)^{2|z_H|} \quad (10)$$

For the sake of completeness we may easily obtain from Eq. (6) an expression to be used when the surface potential is below 25 mV and the ionic strength is so low that the semi-infinite geometry cannot be used. In this case, the surface potential can be related to the surface concentration of the lipophilic ion via a solution of the linearized Poisson–Boltzman equation in cylindrical coordinates [12]:

$$\Psi^\circ = \frac{[\mathrm{LH}]z_\mathrm{H}F}{\kappa\varepsilon_0\varepsilon_\mathrm{r}}\frac{I_0(\kappa r)}{I_1(\kappa r)} \quad (11)$$

where $I_0(\kappa r)$ and $I_1(\kappa r)$ are the modified Bessel function of the first kind of order zero and one, respectively and r is the pore radius of the stationary phase, and κ is the inverse Debye length. When Eq. (11) is introduced in Eq. (6) the following expression is obtained.

$$[\mathrm{H}] = \frac{\mathrm{LH}}{K_\mathrm{LH}(L_\mathrm{T} - \mathrm{LH})}\exp\left(K_2\frac{\mathrm{LH}}{A}\right) \quad (12)$$

where K_2 is

$$K_2 = \frac{z_H^2 F^2}{\kappa\varepsilon_0\varepsilon_r RT}\frac{I_0(\kappa r)}{I_1(\kappa r)} \quad (13)$$

Eq. (12) improves the approach followed by Stahlberg and co-workers, since it avoids the linearization of the isotherm. The field of application of Eqs. (10) and (12) is complementary, even if, in the chromatographic practice, experimental conditions are such that Eq. (10) is likely to be more helpful.

The next logical step is to investigate whether, under particular experimental conditions that actually allow the linearization of Eq. (5), the chromatographically accessible area of the packing can be found via a procedure easier than those already developed [12,14]. It can be demonstrated that the Freundlich adsorption isotherm can be obtained from the linearized potential modified Langmuir adsorption isotherm. This holds true for lipophilic ions because the adsorption energy depends in a logarithmic way on the surface concentration of the adsorbate; the electrostatic repulsion between adsorbed ions and the incoming ion of the same species runs counter to their further adsorption. Its use is not empirical if the linearization of Eq. (5) is acceptable and if the surface potential is high since in this case we may approximate $\sinh^{-1}(x) = \ln[x + (x^2 + 1)^{0.5}] \approx \ln(2x)$ [15,17]. In this case, at constant ionic strength we have the following isotherm:

$$[\mathrm{LH}] = a[\mathrm{H}]^b \quad (14)$$

or

$$\mathrm{LH} = Aa[\mathrm{H}]^b \quad (15)$$

when [LH] is in molecules/cm^2 and [H] is M we have $a = 5.51 \times 10^{13}\exp(W/RT)c_i^{1/3}$, $b = 1/3$ at 20 °C. The constant a depends on the dielectric constant of the medium, on the temperature, on the energy of adsorption of a –CH2– group of the lipophilic chain, at the water/oil interface (W) [15,18], and on the electrolyte concentration (c_i). Since a and b are known, the only adjustable parameter in Eq. (15)

is A and it can be found from the fitting of experimental data. Eq. (12) is much simpler than Eq. (10). Actually, the second assumption made to obtain the Freundlich isotherm (surface potential higher than 100 mV, not easily reached if the concentration of the amphiphilic ion is very low) is hardly compatible with the linearization of the isotherm that would require an amphiphile concentration approaching zero. Hence, the use of the Freundlich equation is often semi-empirical. If experimental conditions are such that the approximations made do not properly apply, the constants a and b are different from the theoretical ones; nevertheless, the general form of the isotherm still holds true and it is of strong practical value. If b is left as a fitting parameter and its estimate is close to 1/3, one can reasonably conclude that the assumptions are acceptable [15].

3. Results and discussion

We will use raw data in refs. [12,14] to expand and critically examine the earlier theoretical work.

Fittings were performed using the software MacCurveFit 1.5.4 (1991–2000), Kevin Raner Software. The molecular area was calculated using the AM1 theory.

Let us start with the experimental adsorption isotherms of p-toluenesulfonate (PTS) in ref. [14]. They were obtained from breakthrough experiments at constant total ionic strength on a polystyrene-divinylbenzene resin (MPIC, Dionex). The area measured by the BET method, according to the manufacturer, was ~400 m²/g. The authors' approach gave 93 m²/g. The average pore diameter of the resin was ~70 Å. The Debye lengths were 9.6, 13.5, 19.1 to 24.7 Å, for eluents of 100, 50, 25, 15 mM ionic strength. It follows that the semi-infinite geometry properly applies only for an eluent of 100 mM ionic strength, hence, to test the present theory, we will use only adsorption data at $I = 100$ mM. From the eluent composition, f (Eq. (8)) was 2.61 μmol/m². The fit of Eq. (10) to this isotherm was successfully performed and it is shown in Fig. 1. The correlation coefficient was 0.9998. The model accounts quite well for the curvature of the data. The mean percent error for the [H] estimate is 3.61% (quite low, compared to the experimental error). It has to be emphasised that the highest individual error is obtained for the first non-zero point. This is probably due to the higher experimental error that is made when the PTSA concentration is very low (see the discussion as regards the approximations made to obtain the adsorption isotherms in ref. [14]).

The best estimates of the adjustable parameters are 181 m² for A (134 m²/g), 0.293 mM⁻¹ for K_{LH}, and 192 μmol for L_T. These results were obtained under the assumption that anionic sites native to the resin may be negligible with respect to L_T. Actually, they are a fraction of the polar impurities of the resin [19–21] (which were demonstrated to be the vinyl groups, above all [20]). We deliberately did not take them into account to keep the number of adjustable parameters
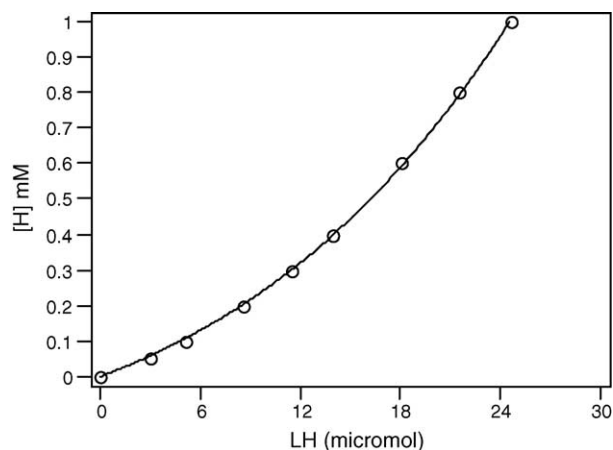

Fig. 1. Experimental (points) and theoretical (solid line) adsorption isotherm of p-toluensulphonate for a column packed with MPIC resin. Raw data are taken from ref. [14]. Eq. (10) was used to fit the raw data. [H], concentration of p-toluensulphonate in the eluent (mM); LH, amount of p-toluensulphonate adsorbed onto the stationary phase (μmol). Eluent: sodium chloride, $I = 100$ mM, $T = 295$ K.

at a minimum. Interestingly the value for the native anionic sites on the resin found by the cited authors' approach was 7.6 μmol; even if we may consider this value as a tentative estimate for the reasons explained below, it is negligible with respect to the present estimate of L_T and thereby indirectly confirms our assumption. Since $[L_T] = L_T/A = 1.1$ μmol/m², the area occupied by a single PTS ion is 151 Å². This value is slightly higher than the molecular surface of PTS, found by the software calculation of the molecular area (87 Å²). This result was easily predictable, since a very close packing of the PTS ions is not possible: sodium counterions are not adsorbophilic, hence the PTS ions experience electrostatic repulsion. It should be pointed out that the chromatographic packing area estimated by the present model (134 m²/g) is ca. one third of the area found by N₂ sorptometry. This is a realistic result if the pore diameter distribution of the material is taken into account. The aromatic ring makes PTS quite a rigid molecule. We may expect that PTS ions would not to be able to enter the porous space if the pore size compares to the PTS molecular length. Probably, the agreement between N₂ sorptometry and the results obtained by the present method would be higher for larger pore sizes or for hypothetical material without micro-pores and cracks, inaccessible for larger adsorbates.

The fitted value for K_{LH} corresponds to $\Delta G° = -14.08$ kJ/mol which is a very reasonable value for the standard free energy of an IIR adsorption [15,18]. We also find that the term K_{LH} [H] $\exp(-z_H F\Psi°/RT)$ in Eq. (5) was as large as 0.15, and that is not negligible with respect to one, hence the linearization of Eq. (5), that is the presupposition to obtain the equation fitted by the cited authors to their experimental data [14], is not feasible, as anticipated. This can be confirmed from the percentage of L_T covered by the highest number of adsorbed PTS; this corresponds to 13% that is obviously not negligible. The

validity of their approach can also be questioned if one also takes into also account the fact that the G–C theory equation for a semi-infinite geometry was not properly used for most of their experimental data (surely for isotherms obtained at $I = 15$ and 25 mM [16]). Hence, it is possible to understand why their theoretical model does not fully account for the curvature [14]. The bare fitting of experimental data does not imply the adequacy of the model. In this context it is worthwhile to anticipate that if a linearized isotherm is used when it does not hold, the model estimates a lower area to amend this. We wish to emphasize that the use of the linearized isotherm does not allow one to find the best estimates of the thermodynamic equilibrium constant for the adsorption of H (K_{LH}) and the total ligand site concentration [L_T] separately. Correctly, the authors conclude that there is no way to quantitatively confirm how good the linearization approximation is from fitting experiments. We have quantitatively demonstrated that it was absolutely not acceptable, as could have been predicted on the basis of the authors' remark on the strong adsorbophilicity of PTS on their resin.

Let us comment on the adsorption isotherms of PTS onto a LiChrospher 100 RP phase (Merk) in Fig. 1 of ref. [12]. The phase has a pore diameter of 100 Å, hence the semi-infinite geometry surely applies for $I = 100$ mM (Debye length 9.6 Å) and probably also for $I = 50$ mM (Debye length 13.6 Å), but not for the eluent of 25 mM ionic strength (Debye length 19.2 Å). The area measured by the BET method, according to the manufacturer, was 350 m^2/g. The authors' approach gave a surface area of ca. 230 m^2/g. From the eluent composition, f (Eq. (8)) was 2.60 μmol/m^2. The fit of Eq. (10) to the isotherm obtained at 100 mM ionic strength for which the semi-infinite geometry properly applies, was successfully performed and it is shown in Fig. 2. The correlation coefficient was 0.9999. The mean percent error for the [H] estimate
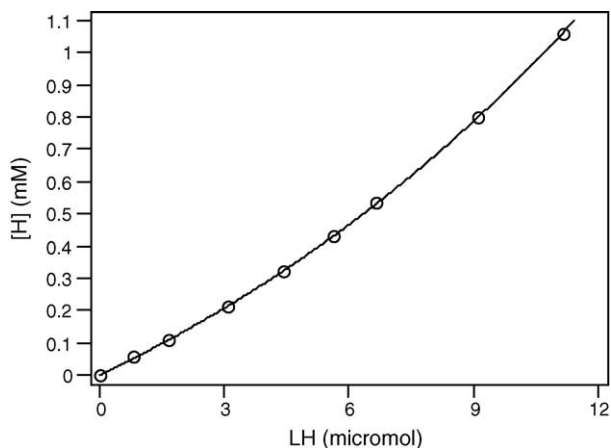

Fig. 2. Experimental (points) and theoretical (solid line) adsorption isotherm of *p*-toluensulphonate for a column packed with LiChrospher RP-18. Raw data are taken from ref. [12]. Eq. (10) was used to fit the raw data. [H], concentration of *p*-toluensulphonate in the eluent (mM); LH, amount of *p*-toluensulphonate adsorbed onto the stationary phase (μmol). Eluent: phosphate buffer pH 3, $I = 100$ mM, $T = 298$ K.

is as low as 0.96%. Again, for similar reasons, the highest individual error is obtained for the first non-zero point. The best estimates of the adjustable parameters are 168 m^2 for A (280 m^2/g), 0.133 mM^{-1} for K_{LH}, and 122 μmol for L_T. It should be pointed out that the best estimate of the chromatographic packing area (280 m^2/g) is lower than the area found by N$_2$ sorptometry. It is noteworthy that the agreement between surface areas determined by N$_2$ sorptometry and the present method is higher compared to surface area determination for PTS adsorption data on the styrene-divinylbenzene resin [14]; as anticipated, this is probably due to the pore size that is larger for the Lichrospher 100 PR material.

The fitted value for K_{LH} corresponds to $\Delta G° = -12.13$ kJ/mol which is slightly lower than the value obtained for PTS with the styrene-divinylbenzene resin (see above, -14.08 kJ/mol). This is in agreement with the already noted stronger adsorbophilic attitude of PTS onto the resin compared to the silica-base packing [14]. With regard to the feasibility of the linearization of Eq. (5), we found that the term K_{LH} [H] exp($-z_H F\Psi°/RT$) was as large as 0.10, that is not completely negligible with respect to one (10%), and hence the linearization of Eq. (5), i.e. the presupposition required to obtain the equation the authors fitted to their experimental data, is not feasible since the denominator is 1.10. In light of the above mentioned PTS surface area calculation (87 Å^2), and taking into account the electrostatic repulsion that prevents a very close packing, the value of amphiphile surface area (50 Å^2), considered by the authors to obtain a denominator of 1.07, seems to be too low; hence the monolayer capacity they obtained was probably higher than the real one, and the denominator was underestimated. This can be confirmed by the percentage of L_T covered by the highest number of adsorbed PTS; this corresponds to 9.1% that is obviously not negligible. It is possible to understand why the chromatographic packing area estimated by the authors' approach (the highest value was 230 m^2/g) was lower than the present one. In Eq. (14) of ref. [12], the right-hand member should have been divided by the real denominator of the adsorption isotherm that is not 1.00 but 1.10. It follows that the right-hand member of Eq. (19) of Ref. [12] lacks a small positive amount. Since the model does not account for this, a lower area is obtained. The same reasoning applies to Eq. (5) of ref. [14] as anticipated, and concurs to elucidate why the authors found such a low resin surface area. Since for all the three data sets of ref. [12], the surface potential is below 25 mV, the use of Eq. (11) to relate the surface potential to [LH] is acceptable, it follows that Eq. (12) should give a good estimate of the surface area. From the fitting, it is found that these estimates are 169, 165 and 166 m^2, respectively for the mobile phases with ionic strength of 100, 50 and 25 mM. The good adherence among these estimates and the agreement with the estimate obtained from the fitting of the data set at $I = 100$ mM by Eq. (10) (168 m^2) attest the importance of the use of the non-linearized isotherm in the theory cultivated here.

4. Critical comparison of the methods to determine the packing surface area via the adsorption isotherm of lipophilic ions

To fulfil IUPAC recommendations as regards surface characterisation methods [22], the most eligible method depends on the specific application: the former should be closely related to the latter. The present approach, that involves lipophilic ions adsorption, is suitable, since IIC is founded precisely on this phenomenon. The best probe to determine the packing area accessible to the IIR would be the IIR itself, also because the recording of its adsorption isotherm is necessary to use retention equations and to perform educated guess. This way the chromatographer will have a double advantage.

The main improvement of the present development of the theory is the use of the integral form of the electrostatically modified Langmuir adsorption isotherm. This must be used when the amphiphilic concentration range is chromatographically meaningful [10], but we have quantitatively demonstrated that, even if the amphiphile concentration approaches zero, the linearization is hardly practicable. This questions the validity of the first assumption of both the approaches in refs. [12,14]. The lower the feasibility of the linearization, the lower is the estimated surface area. It is rewarding to observe that our estimates of the chromatographically accessible surface areas are higher than those provided by earlier methods [12,14]. From a careful review of the most reliable literature data [2–11] we have realised that the linearization of the isotherm is a critical issue for the theory, as also pointed out in refs. [7,10], particularly if the amphiphile is negatively charged; hence we advise against the use of the linearized adsorption isotherm even if the amphiphile concentration is very low. Noteworthy, our model allows one to decide whether the linearized potential modified Langmuir adsorption isotherm can be properly used, and this is extremely important if this adsorption isotherm has to be included in retention model equations.

In the amphiphile concentration range used in chromatographic practice, the surface potential is rarely below 25 mV [2–11] and hence the second approximation in ref. [12] is rarely acceptable chromatographically. Since the experimental set-up for ionized samples usually involves a buffered mobile phase, when the ionic strength is not very low, the use of the cylindrical co-ordinates can be avoided [16], and typical potentials (higher than 25 mV) can be related to the surface concentration of the amphiphile via the G-C expression. Should the potential and the ionic strength be so low that Eq. (11) properly applies, Eq. (12) enpowers the approach followed by Stahlberg and co-workers because it does not involve the linearization of the adsorption isotherm.

Taking into account the limits of applicability of these concepts, we believe that the proper approximation to express the surface potential can be made according to the experimental conditions, but the isotherm should never be linearized, also because Eqs. (10) and (12) are not algebraically difficult. These expressions are complementary, as regards the approximations made to obtain them hence the field of their application is actually very wide.

In conclusion the present method capitalizes on the attractive approach of using the adsorption isotherm to determine the chromatographically accessible surface area of stationary phases. This physical area is more relevant to model makers in the field of ionic adsorption from solution (IC, IIC), but also to the phase ratio determination [12]. We believe that this procedure is to be preferred to the BET method, according to the IUPAC recommendations regarding surface characterisation methods. The correctness of the physical description of the theory is witnessed by its ability to quantitatively describe the system via adjustable parameters with a clear chromatographic meaning and reliable estimates.

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