



# Surface area determination of a polystyrene–divinylbenzene chromatographic packing material via ionic amphiphile adsorption from aqueous mobile phases and application of Gouy–Chapman theory

Travis L. Niederhauser, David H. Scoville, John D. Lamb\*

*Department of Chemistry and Biochemistry, Brigham Young University, C100 Benson Science Building, P.O. Box 25700, Provo, UT 84602-5700, USA*

Received 11 February 2002; received in revised form 11 September 2002; accepted 11 September 2002

## Abstract

A method for the determination of the chromatographically accessible area of a reversed-phase column similar to the method of Hägglund and Ståhlberg [J. Chromatogr. A 761 (1997) 13] is applied to a column containing a polystyrene–divinylbenzene resin. Its theoretical basis is Gouy–Chapman theory in combination with an electrostatically modified linear adsorption isotherm. The surface area value determined for the resin,  $96 \text{ m}^2/\text{g}$ , is much less than the reported surface area value,  $400 \text{ m}^2/\text{g}$ , determined by  $\text{N}_2$  sorptometry and application of Brunauer–Emmett–Teller (BET) theory. The method also provides a value for the number of moles of native anionic sites present on the column.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Surface area determination; Stationary phases, LC; Adsorption isotherms; Polystyrene–divinylbenzene

## 1. Introduction

The prevalent technique for the surface area determination of reversed-phase chromatography packing materials is  $\text{N}_2$  sorptometry and application of Brunauer–Emmett–Teller (BET) theory. New methods for the determination of the surface area of hydrophobic packing materials via the adsorption of molecular probes from the liquid phase have recently been presented. Adsorption of  $\text{CCl}_4$  from nonpolar

solvents to silica gels has been quantitatively described with the simple Ono–Kondo lattice cell model by Tolmachev and co-workers [1]. The results were consistent with the BET surface areas for the silica gels. Adsorption of ionic amphiphiles from aqueous solution to octadecyl-bonded silica has been quantitatively described with an electrostatic model by Hägglund and Ståhlberg [2]. They reported a surface area much lower than the BET surface area. In this paper we report the determination of the surface area of a polystyrene–divinyl benzene resin using a modified version of the method of Hägglund and Ståhlberg. We obtained for the resin a surface area value much lower than the BET surface area for the resin. The theoretical basis for the modified

\*Corresponding author. Tel.: +1-801-422-3145; fax: +1-801-422-5474.

E-mail address: [john\\_lamb@byu.edu](mailto:john_lamb@byu.edu) (J.D. Lamb).

version is Gouy–Chapman (G–C) theory and the linearized Langmuir isotherm.

The impetus for this research was the attainment of a surface area value that may be used as a parameter in an explicit retention model based on G–C theory for macrocycle-based ion chromatography carried out on the polymeric resin [3,4]. Our surface area determination method, based on that Hägglund and Ståhlberg, is likely to be more relevant to theoretical modeling of ion chromatography (IC) than the BET surface area because the adsorption processes that occur in our method are more closely related to IC adsorption processes than those of nitrogen sorptometry. This view is based on the general philosophy presented in a recent IUPAC report concerning the selection of an appropriate surface characterization method for a given application. The report advises that a method be chosen that assesses “a parameter *related as directly as possible* to phenomena involved in the application . . . [It] may often be advisable to select a method involving physical phenomena similar or close to those involved during the practical application” [5]. IC and the general surface area determination method of Hägglund and Ståhlberg are closely related because they both involve adsorption of ionic solutes from solution to the stationary phase. The theory of our modified version of their surface area determination method is also compatible with the explicit IC retention model as both are based on G–C theory.

To determine the surface area of the packing on a reversed-phase column by the general method of Hägglund and Ståhlberg, a series of breakthrough experiments are performed with an amphiphile, such as *p*-toluene sulfonate (PTS). In the series of breakthrough experiments, the concentration of the amphiphile is increased from experiment to experiment, while the total ionic strength of the eluents is maintained at a constant value. From the results of these breakthrough experiments, an adsorption isotherm is obtained for the amphiphile. The surface area value is obtained from the fit of the theoretical model describing the system to the experimental data. It is convenient to plot the adsorption isotherm in the form  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus  $N_{\text{WP}}$  where  $N_{\text{WP}}$  is the number of moles of amphiphile adsorbed to the hydrophobic surface and  $c_{\text{W,E}}$  is the concentration of

amphiphile in the bulk eluent. Hägglund and Ståhlberg’s theoretical model of the system predicts that the plot of  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus  $N_{\text{WP}}$  will be a straight line. The slope of the line established by the data points is inversely proportional to the surface area of the column. In their work with an octadecyl-bonded silica column, there was very good correlation between the measured adsorption isotherms and the theoretical fits.

In this work, in the adsorption of PTS to a column packed with the polystyrene–divinylbenzene resin, plots of  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus  $N_{\text{WP}}$  are not straight, but show slight upward curvature. Our theoretical adsorption model can at least partially account for the observed curvature. One of the approximations made in the adsorption model of Hägglund and Ståhlberg is that at constant ionic strength a linear relationship exists between  $\psi_0$ , the electrostatic potential at the surface, and  $N_{\text{WP}}$ , the number of moles of amphiphile adsorbed to the hydrophobic surface. This approximation is considered valid when  $\psi_0$  is small. For our system we calculate values for  $\psi_0$  as large as  $-36$  mV. Consequently, that approximation may not always be appropriate for our system. For our system, two factors contribute to large values of  $\psi_0$ . The first is that PTS has a high affinity for the polymeric resin. We observe twice as much PTS adsorption on the resin-packed column as Hägglund and Ståhlberg observed on their octadecyl-bonded silica column under similar conditions, even though the calculated surface areas of the two columns were similar. The second reason is that the resin itself contains native anionic sites that contribute to  $\psi_0$  [3]. Native anionic sites on polystyrene–divinyl benzene resin has been noted by another group as well [6]. Our theoretical model for amphiphile adsorption takes into account the possibility of a native surface charge and incorporates the full G–C theory equation for  $\psi_0$  that allows for a non-linear relationship between surface charge and  $\psi_0$ .

The surface area value we obtained for the column packing material is  $96 \text{ m}^2/\text{g}$ , whereas the BET surface area value provided by the manufacturer is  $\sim 400 \text{ m}^2/\text{g}$ . In addition to the surface area value, we also obtained values for the number of moles of native anionic sites on the column and for  $N_{\text{p0}}K_{\text{WP}}$ , where  $N_{\text{p0}}$  is the total number of moles of hydro-

phobic adsorption sites on the packing material and  $K_{WP}$  is the equilibrium constant for amphiphile adsorption.

## 2. Theory

The following equilibrium equation represents the adsorption of an amphiphile to a reversed-phase packing material



where  $W^-$  is the amphiphile,  $P$  is the surface adsorption site, and  $WP^-$  is the amphiphile adsorbed to the surface. The Langmuir adsorption isotherm for (1) is:

$$N_{WP} = \frac{N_{P0} K_{WP} c_{w,s}}{1 + K_{WP} c_{w,s}} \quad (2)$$

where  $N_{WP}$  is the number of moles of amphiphile adsorbed to the hydrophobic surface,  $N_{P0}$  is the total number of moles of hydrophobic adsorption sites on the packing material, and  $c_{w,s}$  is the solution concentration of the amphiphile at the surface. The parameter  $c_{w,s}$  is related to  $c_{w,e}$ , the concentration of the amphiphile in bulk solution, by the Boltzmann equation:

$$c_{w,s} = c_{w,e} \exp\left(\frac{-z_w F \psi_0}{RT}\right) \quad (3)$$

where  $z_w$  is the charge of the amphiphile,  $F$  is the Faraday constant,  $\psi_0$  is the electrostatic potential at the surface,  $R$  is the gas constant, and  $T$  is the absolute temperature. This description of amphiphile adsorption parallels the electrostatic description of ion interaction reagent adsorption in ion interaction chromatography [7,8].

As the bulk solution concentration of the amphiphile approaches zero, the denominator of Eq. (2) approaches one. For low values of  $c_{w,s}$ , the denominator of Eq. (2) can be approximated by one to give the linearized adsorption isotherm:

$$N_{WP} = N_{P0} K_{WP} c_{w,s} \quad (4)$$

Substitution of Eq. (3) into Eq. (4) and rearrangement yields:

$$\frac{N_{WP}}{c_{w,e}} = N_{P0} K_{WP} \exp\left(\frac{-z_w F \psi_0}{RT}\right) \quad (5)$$

Taking the log of both sides of (5) and substituting  $-1$  for  $z_w$  gives:

$$\ln\left(\frac{N_{WP}}{c_{w,e}}\right) = \ln(N_{P0} K_{WP}) + \frac{F \psi_0}{RT} \quad (6)$$

The next step is to incorporate into Eq. (6) an expression for  $\psi_0$ . Hägglund and Ståhlberg define  $\psi_0$  with a solution of the linearized Poisson–Boltzmann equation in cylindrical coordinates [9]. We have chosen to define  $\psi_0$  in this work using G–C theory because G–C theory is the basis of the explicit IC retention model in which the surface area value is used [3].

Within G–C theory we considered two options for defining  $\psi_0$ . One option considered is the equation for  $\psi_0$  incorporating the Debye–Hückel approximation. The other option considered is the full G–C theory equation for  $\psi_0$ . Incorporation of the Debye–Hückel approximation leads to an adsorption model similar to that of Hägglund and Ståhlberg in which there is a linear relationship between  $\ln(N_{WP}/c_{w,e})$  and  $N_{WP}$ . However, as was discussed previously, for our system it is more appropriate to use the full G–C theory equation for  $\psi_0$  for a system containing a symmetrical, univalent electrolyte:

$$\psi_0 = \frac{2RT}{F} \sinh^{-1}\left(\frac{\sigma_0}{\sqrt{8RT\varepsilon_0\varepsilon_r c}}\right) \quad (7)$$

where  $c$  is the concentration of the electrolyte in the bulk solution.

The charge on the surface of the polymeric resin is due both to adsorbed amphiphile and to the anionic sites native to the resin, so  $\sigma_0$  is given by the following equation where  $z_A$  is the charge of the native anionic sites and  $N_{A0}$  is the number of moles of available native anionic sites on the resin in the column:

$$\sigma_0 = \frac{F}{A_S}(z_w N_{WP} + z_A N_{A0}) \quad (8)$$

Eqs. (6)–(8) are combined and the resulting equation

is fit to the experimental adsorption isotherms plotted in the form  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus  $N_{\text{WP}}$ :

$$\ln\left(\frac{N_{\text{WP}}}{c_{\text{W,E}}}\right) = \ln(N_{\text{P0}}K_{\text{WP}}) + 2 \sinh^{-1}\left(\frac{F(z_{\text{w}}N_{\text{WP}} + z_{\text{A}}N_{\text{A0}})}{A_{\text{S}}\sqrt{8RT\varepsilon_0\varepsilon_{\text{r}}c}}\right) \quad (9)$$

### 3. Experimental

#### 3.1. Eluent preparation

A stock solution of 64.6 mM sodium *p*-toluenesulfonate, pH 7.0, was prepared from toluene sulfonic acid (98.5%, Aldrich, Milwaukee, WI, USA), and standardized NaOH and HCl solutions. Three eluent sets of nine aqueous eluents each were prepared from the *p*-toluenesulfonate (PTS) stock solution and a sodium chloride stock solution. Each set contained solutions of the following concentrations of PTS: 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1 mM. The solutions in the first set were all of 25 mM ionic strength. The solutions in the second set were all of 50 mM ionic strength. The solutions in the third set were all of 100 mM ionic strength. Also, a set of eluents of 15 mM ionic strength with the following concentrations of PTS were prepared: 0, 0.05, 0.1, 0.15, 0.25, and 0.35 mM. In calculating the amount of sodium chloride stock solution to add to bring the solutions to the appropriate ionic strength, the PTS concentrations were taken into account.

A set of 50 mM ionic strength buffered PTS eluents were prepared starting with different stock solutions. The procedures for preparation of this eluent set and the required stock solutions were similar to the procedures for preparation of the aforementioned stock solutions and the 50 mM ionic strength eluent set. However, in addition, each eluent in the set was prepared to contain 0.099 mM sodium monohydrogen phosphate (analytical concentration) and 0.10 mM sodium dihydrogen phosphate (analytical concentration). The concentration of the phosphate buffer present was intentionally kept low so that its contribution to the ionic strength and the properties of the double layer could be neglected.

#### 3.2. Experimental set-up

A DX500 chromatograph (Dionex, Sunnyvale, CA, USA) was used in conjunction with an AD20 absorbance detector (Dionex). For the holdup volume determination experiments with sodium nitrate solutions, the absorbance detector wavelength was usually set to 275 or 300 nm. For PTS breakthrough experiments, the wavelength was usually set to 235 nm. The chromatography column used was a 4 × 250-mm column packed in-house. The column was packed with ~1.35 g MPIC resin. (Dionex, diameter: 10 μm, ~400 m<sup>2</sup>/g, Nitrogen sorptometry results provided by the manufacture suggests that the majority of the pores have diameters < ~19 nm with an average pore diameter of ~7 nm.) To prepare the resin slurry, 2 g MPIC resin were mixed with 4 ml water and 4 ml methanol. The methanol was evaporated off at ambient temperature while stirring. The slurry was brought up to a volume of 30 ml with 0.1 M NaOH. The packing solution was 0.1 M NaOH and the slurry chamber temperature was 60 °C. The column was packed for 10 min at a pressure of 379 bar.

#### 3.3. Breakthrough experiments

Breakthrough experiments for a given eluent set were carried out in a sequential stepwise fashion. The column was first flushed with the eluent (in the set) containing no PTS. In subsequent experiments a switch was made from the previous eluent to the eluent containing the next highest concentration of PTS. Breakthrough experiments for holdup volume determination were performed for each eluent set by switching from the eluent (in the set) containing no PTS to an eluent of the same ionic strength containing 5 mM nitrate. Differences in the measured holdup volumes were observed, indicative of nitrate exclusion from the diffuse layer due to the native anionic sites on the packing material. These differences were small in comparison with the breakthrough volumes of PTS. These holdup volume values were used in calculations as this nitrate exclusion partially compensated for the exclusion of PTS from the diffuse layer, which was not taken into account in the model for reasons described below.

#### 4. Results and discussion

The adsorption isotherms for PTS at four different ionic strengths are shown in Fig. 1. Fig. 1A shows the adsorption isotherms represented in the typical manner, whereas Fig. 1B shows the same adsorption isotherms in the form  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus  $N_{\text{WP}}$ , where  $N_{\text{WP}}$  is the number of moles of amphiphile adsorbed to the surface and  $c_{\text{W,E}}$  is the concentration of the amphiphile in the bulk eluent. The solid circles in Fig. 1 are the experimental data points, and the lines are the theoretical fits obtained with Eq. (9). Curve fitting was carried out using a variance minimization algorithm. All four adsorption isotherms represented in the form  $\ln(N_{\text{WP}}/c_{\text{W,E}})$  versus

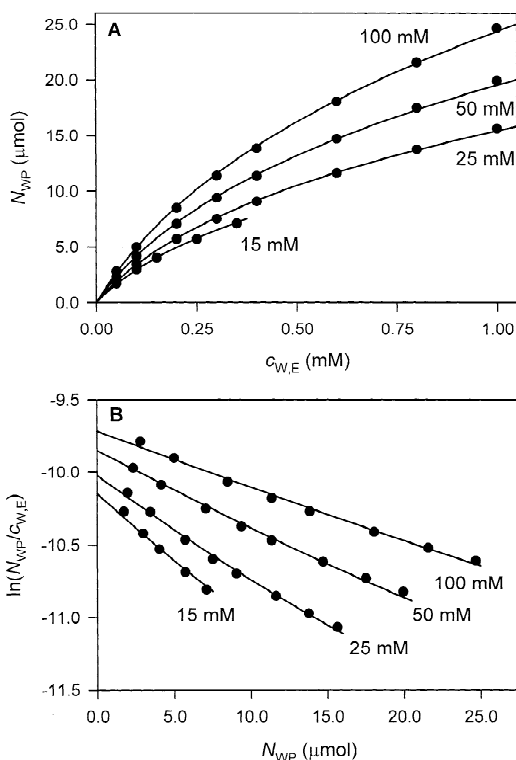


Fig. 1. Experimental (●) and theoretical (solid line) adsorption isotherms of *p*-toluenesulfonate for a column packed with MPIC resin. (A) Adsorption isotherms represented in the traditional manner; (B) adsorption isotherms represented in the manner of Hägglund and Ståhlberg;  $N_{\text{WP}}$ , amount of *p*-toluenesulfonate adsorbed to the column;  $c_{\text{W,E}}$ , concentration of *p*-toluenesulfonate in the bulk eluent. Eluents: sodium chloride solutions of ionic strengths of 15, 25, 50 and 100 mM.  $T=295$  K,  $\epsilon_r=78$ .

$N_{\text{WP}}$  were fit simultaneously, and one set of parameters for all four adsorption isotherms was obtained. Curve fitting was carried out multiple times starting with different sets of initial values for the fitted parameters. The theoretical fit shown in Fig. 1 is that which yielded the smallest sum of errors squared. The fitted parameters are:  $A_s$ , the column packing surface area;  $N_{\text{A0}}$ , the number of moles of anionic sites native to the resin on the packing surface; and for each adsorption isotherm, an individual parameter for  $\ln(N_{\text{P0}}K_{\text{WP}})$ . Given the fitted value for  $N_{\text{A0}}$ ,  $\psi_0$  can be determined from Eqs. (7) and (8).

While it is clear that the adsorption model does not fully account for the curvature observed in the experimental data in Fig. 1B, the fit to the experimental data in Fig. 1 is quite good. Also, the values for the fitted parameters are internally consistent. The fitted value for  $A_s$  is  $130 \text{ m}^2$  ( $96 \text{ m}^2/\text{g}$ ). It is substantially less than the BET surface area of the column,  $540 \text{ m}^2$  ( $400 \text{ m}^2/\text{g}$ ), and greater than  $1.4 \text{ m}^2$ , the calculated surface area for smooth close-packed  $10\text{-}\mu\text{m}$  spheres occupying a  $4 \times 250\text{-mm}$  chromatography column. The fitted value for  $N_{\text{A0}}$  is  $7.6 \times 10^{-6} \text{ mol}$ . Notably, for each isotherm, the fitted value of  $\ln(N_{\text{P0}}K_{\text{WP}})$  is  $-9.4$ . For comparison purposes, in our model we replaced the G–C theory equation for  $\psi_0$  with the linearized equation for  $\psi_0$  employed in the model of Hägglund and Ståhlberg [2]. After curve fitting our experimental data with the modified model we obtained a surface area value of  $210 \text{ m}^2$ . The new fit to the experimental data was not as good as the fit shown in Fig. 1.

None of the eluents used to obtain the results in Fig. 1 were buffered. The pH values of the eluents used to obtain the 15 mM ionic strength breakthrough curve were measured and the pH values for the six eluents ranged from 6.3 to 8.5. In order to investigate whether the change in pH among the eluents used influenced the amount of PTS adsorbed, a PTS adsorption isotherm was obtained with buffered eluents with ionic strengths of 50 mM, and the results were compared with the 50 mM ionic strength adsorption isotherm shown in Fig. 1B. The buffered eluents contained 0.2 mM phosphate and the pH values of the final eluents ranged from 6.9 to 7.3. The two isotherms were very similar, which suggests that the  $\text{p}K_{\text{a}}$  or  $\text{p}K_{\text{a}}$  values of the native anionic sites are not in the pH range of the eluents used to obtain

the adsorption isotherms of Fig. 1. If the  $pK_a$  of a population of acidic sites on the column were close to the pH of the eluent in the column and the eluent was switched to one of a different pH, then the population of native acidic sites in the ionic form would change. This would influence  $\psi_0$  which in turn would affect the amount of PTS adsorbed to the surface.

A major approximation made in the derivation of Eq. (9), the equation that is fit to the experimental adsorption data, is the linearization of the adsorption isotherm (Eqs. (2) and (4)). With linearization, the assumption is made that the denominator of Eq. (2) approximates 1. Unfortunately, there is no way to mathematically evaluate how well the denominator of Eq. (2) approximates 1 from the information obtained from these curve fitting experiments. The denominator of Eq. (2) cannot be calculated without knowing either  $N_{p0}$  or  $K_{WP}$ . The curve-fitting experiments provide a value for  $N_{p0}K_{WP}$ , but not for  $N_{p0}$  or  $K_{WP}$  individually. Additional experiments, perhaps of a different sort, need to be performed to determine either of these values individually. Consequently, the value of  $N_{WP}$  beyond which the linearized Langmuir isotherm is not valid is not known. The good theoretical fits to the experimental data in Fig. 1 suggest that the experimental data lie mainly in the portion of the adsorption isotherm that is acceptably represented by the linearized adsorption isotherm of Eq. (4).

Another approximation of the adsorption model is the neglect of exclusion of the amphiphile from the diffuse layer due to the negative value for  $\psi_0$ . Experimentally, amphiphile exclusion was partially compensated for by the use of nitrate as a holdup volume marker, which also experienced exclusion due to the native anionic sites on the packing material surface. From theory, diffuse layer accumu-

lation of the amphiphile has been taken into account, and calculations have been carried out that indicate for this work that the exclusion from the diffuse layer is a negligible contributor to overall adsorption. Hägglund and Ståhlberg arrived at the same conclusion for their research [2].

The general surface area determination method described in this paper and in Hägglund and Ståhlberg's work is new. The method may prove to be a good alternative to the BET method in many circumstances where adsorption of ions from liquids to hydrophobic solids is of interest.

### Acknowledgements

The authors gratefully acknowledge the financial support of Dionex Corporation.

### References

- [1] N.G. Kryuchenkova, T.A. Kuznetsova, M.V. Borodulina, E.N. Egorov, A.M. Tolmachev, Russ. J. Phys. Chem. (Engl. Transl.) 75 (2001) 1210.
- [2] I. Hägglund, J. Ståhlberg, J. Chromatogr. A 761 (1997) 13.
- [3] T.L. Niederhauser, R.A. Lochhead, D.H. Scoville, J.D. Lamb, J. Chromatogr. A (2002) submitted.
- [4] T.L. Niederhauser. Macrocyclic-based anion chromatography: I. A mathematical model for anion retention. II. Carbohydrate separations. Dissertation, Brigham Young University, Provo, UT, 2000.
- [5] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing, K.K. Unger, Pure Appl. Chem. 66 (1994) 1739.
- [6] S. Puon, F.F. Cantwell, Anal. Chem. 49 (1977) 1256.
- [7] J.-G. Chen, S.G. Weber, L.L. Glavina, F.F. Cantwell, J. Chromatogr. A 656 (1993) 549.
- [8] J. Ståhlberg, J. Chromatogr. A 855 (1999) 3.
- [9] R.E. Rice, F.H. Home, J. Colloid Interface Sci. 105 (1985) 172.