

Surface Area Measurements with Linear Adsorbates: An Experimental Comparison of Different Theoretical Approaches

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Received March 4, 2009. Revised Manuscript Received April 15, 2009

The specific area of a substrate was determined from the results of adsorption isotherms performed with a sequence of four alkanes, from methane to butane, using three different approaches. The data were first analyzed using the BET equation and the point B methods; these results were compared with those obtained using a new equation designed for examining the case of multisite occupancy. The new model specifically accounts for sites that are left uncovered in the case of adsorption by linear adsorbates. Of these three, only the last method gives essentially the same value for the specific surface area of the substrate when different adsorbates are used to measure it. The other two, more traditional, approaches give values of the specific surface area that decrease as the length of the adsorbate used increases.

I. Introduction

The specific surface area is an important property used to characterize an adsorbent. The most widely used approach to determine this quantity is to measure an adsorption isotherm, typically with N₂ gas at 77 K, and then to fit the resulting data to the BET equation over an appropriate range of pressures.^{1,2} The BET equation² yields a value for the monolayer capacity of the substrate (i.e., the number of molecules needed to form one complete monolayer film on the substrate), and, it provides, as well, a value for a parameter indicative of the strength of the adsorbate–substrate attraction.

The physical model of adsorption behind the BET equation is based on a number of assumptions, some of which are not necessarily well-founded.^{1,3} One of this latter group is the assumption that each adsorbate occupies only one site on the substrate. While this may be true in some special cases, more often it is not.⁴ Even in the simplest of circumstances (e.g., a classical rare gas, such as Kr or Xe, adsorbed on graphite) the size of the adsorbate is greater than the separation between adjacent adsorption sites.⁵ Consequently, when an adsorbate occupies one site, it generally prevents the occupation of several other sites.

The assumption of single-site occupation breaks down even further for linear or quasi-linear molecules. As a result, if the BET equation is used in this case, the values obtained for the area of a given substrate decrease as the length of the linear adsorbates used increases.^{6,7} One would expect that an appropriate model for describing adsorption by linear molecules, by contrast, should yield essentially the same value for the area when adsorbates of various lengths are used to measure it.

Recently, Riccardo, Ramirez, and Roma (or RRR for short) proposed a modification of the BET approach in order to explicitly take into account adsorption by linear molecules.^{6,8} In their calculations the linear molecules were treated as “*k*-mers”; i.e., they consisted of *k* identical units. The RRR approach kept the basic spirit of the BET model (for example, both in the RRR and in the BET approaches it is assumed that the binding is stronger for molecules adsorbed in the first layer than in all the other layers; both in the RRR and in the BET approaches a molecule is only allowed to adsorb in the second layer if it sits exactly on top of a molecule adsorbed in the first layer, with no overhangs; etc.). The new contribution made by the RRR approach was the inclusion of the additional entropy that results from having sites that cannot be occupied when linear molecules, or “*k*-mers”, are present on a substrate.

When the RRR approach was proposed,^{6,8} the results of the model were compared to Ar and N₂ isotherms measured on a nonporous substrate. In order to compare a theoretical model for the adsorption of linear molecules on a 2D surface with experiments, it would be preferable to have a set of isotherms measured using increasingly longer linear molecules on a nonporous substrate. Here we report on such a comparison: We have determined the surface area of the same sample of HiPco nanotubes from adsorption isotherms measured with a sequence of four alkanes (from methane to butane), using both the RRR approach and the BET approach.

Our main finding is that the RRR approach yields essentially the same area for the substrate when molecules of different lengths are used to measure this quantity. The values obtained for the specific area are consistent with those obtained from using the BET approach with spherical adsorbates.

II. Experimental Methods

The single-walled carbon nanotube sample employed in this study was purchased from CNI (Carbon Nanotechnology Inc.). Adsorption isotherms were measured on a sample of purified HiPco nanotubes. The nanotubes were not subjected to any additional treatment other than pumping to a vacuum of better than 1×10^{-6} Torr, for a period of 72 h, prior to the performance

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of each set of measurements. While the purification process to which the nanotubes were subjected by the manufacturer may result in uncapping of a fraction of them, the resulting uncapped tube openings are blocked by chemical functional groups produced during the purification process.⁹ Unblocking the uncapped nanotubes requires heating the sample, under vacuum, to at least 650 K.^{10,11} Thus, access to the interior volume of the nanotubes used in this study was precluded. Adsorption on our sample occurs, overwhelmingly, on the external surface of the bundles (and on a few, large-diameter, defect-induced, interstitial sites present in the bundles).^{12,13}

The adsorption isotherms were measured in an especially designed volumetric adsorption isotherm setup.¹⁴ Low temperatures were produced by a helium closed-cycle refrigerator. The isotherm temperatures were controlled using two temperature controllers. The pressures were measured with three capacitance manometers, having maximum ranges of 1, 10, and 1000 Torr. The pressure gauges are located on the gas-handling unit, at room temperature. The pressures were recorded, and the gas dosing was controlled by a computer running a LabView program written in our laboratory specifically to accomplish these tasks. The gases used in the different experiments were all ultrahigh-purity gases, produced by Matheson Gas.

III. Theoretical Model

The RRR approach was developed in a sequence of two papers. In the first one,⁶ a one-dimensional (1-D) array of adsorption sites was considered. The adsorbate consisted of linear molecules with k identical units (k -mers). There was no attraction between k -mers. A k -mer could only go on the n th layer if it exactly overlapped a k -mer in the next lowest layer, i.e., the $(n - 1)$ th layer. The heat of adsorption in the first layer was different from those in the higher layers; the heat of adsorption in all the higher layers was taken to be that for the adsorbate in the bulk phase. In a second paper the RRR treatment was extended to consider adsorption in two dimensions.⁸ Planar substrates were considered in which the sites were arranged forming square, triangular, or honeycomb lattices. The formalism in ref 8 yields the adsorption isotherm in the multilayer regime from (i) knowledge of an analytical expression for the monolayer adsorption isotherm and from (ii) a mapping from the grand partition function of the monolayer to the grand partition function of the multilayer, where the fugacity of the monolayer transforms into the grand partition function of a single column of k -mers.

The exact 1-D solution in the RRR approach for the monomer case ($k = 1$) corresponds to the BET equation (see eq 1). A closed exact expression was obtained, as well, in the RRR approach in the 1-D case for dimers ($k = 2$) (see eq 2). The problem of determining analytically the adsorption isotherm equation for k -mers on a two-dimensional (2-D) lattice has no closed form solution for $k > 1$. Only approximate expressions exist.^{15–20}

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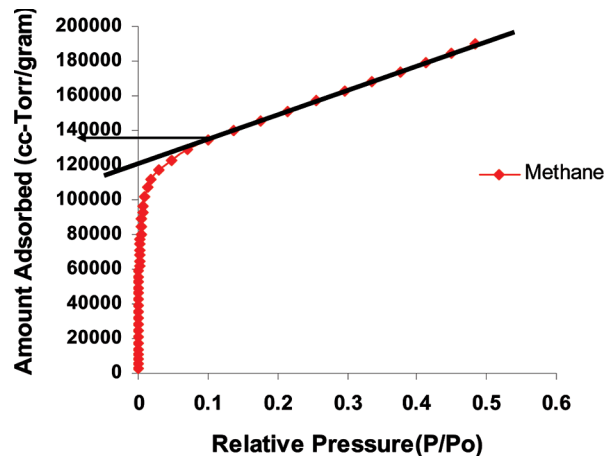


Figure 1. Monolayer isotherm for methane adsorption on single-walled carbon nanotubes. The coverage in $\text{cm}^3 \text{Torr/g}$ (Y axis) is presented as a function of relative pressure (X axis). After a low-pressure region of steep coverage increase there is a region where the coverage increases linearly with pressure; the lowest pressure value where the isotherm deviates from linearity marks the point B, as indicated by the arrow parallel to the X axis in the figure. This point is taken to coincide with monolayer completion.

IV. Results and Discussion

Point B and BET. The experimental values for the area of the HiPco nanotube sample were determined by multiplying the molecular area^{22–25} of the adsorbate times the monolayer capacity of the substrate. The monolayer capacity was obtained from the experimental adsorption isotherms using two different approaches: the BET equation² and the point B method.^{26,27} The values of the specific surface area of the substrate were determined by dividing the experimental value of the area thus computed by the mass of the substrate.

In the point B method, one plots the adsorption isotherm on a linear scale (i.e., the number of adsorbed molecules as a function of pressure). At low pressures, there is a very steep coverage increase with pressure. The steep increase in coverage continues, until eventually a smooth but very sharp bend is reached in the isotherm. This bend is followed by a region in which the coverage increases very little with pressure and does so in an essentially linear fashion. As the coverage is increased further, this linear region ends, and the second layer starts growing on the substrate. The point B is defined as the lowest value of the pressure (and coverage) at which a straight line extrapolation coincides with the experimental data in the linear portion of the isotherm between the first and the second layers.^{26,27} The coverage at the point B corresponds to monolayer completion. The point B method is illustrated in Figure 1. Typically, the values for the monolayer completion obtained from the point B method are larger than those obtained when the monolayer capacity is determined from the BET equation.

Figure 2 displays adsorption isotherms measured for a sequence of alkanes having one, two, three, and four C atoms, respectively (i.e., methane, ethane, propane, and butane) on the same sample of HiPco purified nanotubes. The temperatures at which the isotherms were performed are all different. This is

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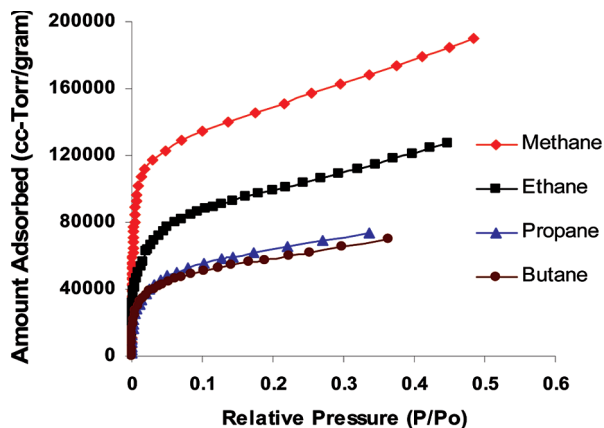


Figure 2. Monolayer isotherms for methane (77.3 K), ethane (165 K), propane (190 K), and butane (220 K) adsorption on single-walled carbon nanotubes. The coverage in $\text{cm}^3 \text{Torr/g}$ (Y axis) is presented as a function of relative pressure (X axis).

required because of the significantly different binding energies that the various alkanes have on the substrate. The temperatures at which the monolayer capacity can be easily determined by methane adsorption are such that the saturated vapor pressures for the other alkane adsorbates are too low to be measured in our setup.^{28,29} Conversely, the temperatures at which the butane monolayer capacity can be readily determined from an isotherm are too high for the monolayer capacity to be measured with methane in our setup²⁹ (the pressures are much too high, and the monolayer range is not readily identifiable for methane under these conditions).

The temperatures at which the isotherms were performed, however, were selected so that when the isotherm temperatures are scaled by the bulk critical temperature corresponding to each adsorbate, (T/T_{c3D}), the resulting scaled temperatures are comparable.

Table 1 lists the molecular areas of the alkanes used. They were obtained from published neutron scattering results for alkane films adsorbed on graphite.^{22–25}

Figure 3 presents plots of the linearized BET equation for the four different adsorbates used. The linearized BET equation is

$$(P/P_0)/[n(1-P/P_0)] = 1/Cn_m + [(C-1)P/P_0]/Cn_m \quad (1)$$

Here P is the pressure of the data point in the adsorption isotherm, P_0 is the saturated vapor pressure for the adsorbate at the isotherm temperature, n is the number of molecules adsorbed at the point of the isotherm corresponding to pressure P , n_m is the monolayer capacity of the substrate, and C is a constant related to the strength of the interaction between adsorbate and substrate.

The range of scaled pressures over which the BET equation is used to obtain n_m typically extends from $P/P_0 \sim 0.05$ to $P/P_0 \sim 0.3$.^{1,2,27} This is the range over which we have plotted the data from the isotherms in Figure 2 to obtain the plots presented in Figure 3.

Figure 4 presents the values of the specific surface area measured on the same HiPco sample, as determined from the point B method and from the BET equation, for the various adsorbates used. It should be noted that the dependence of the specific surface areas determined by these two approaches on the length of the adsorbate molecules is the same: both for the point B method and for the BET equation, as the length of the adsorbate molecules increases, the value of the specific surface

Table 1. Single-Walled Nanotubes Samples and Gases Used in the Isotherm Measurements

sample	type	weight (g)	gas	area/molecule on graphite (\AA^2)	isotherm temp (K)
SWNTs	HiPco	0.1727	methane	15.4 ^a	77
SWNTs	HiPco	0.325	ethane	21 ^b	165
SWNTs	HiPco	0.325	propane	28.8 ^c	190
SWNTs	HiPco	0.325	butane	32.7 ^d	220

^a Reference 22. ^b Reference 23. ^c Reference 24. ^d Reference 25.

area determined for the same sample decreases. The decrease over the range of molecular lengths explored here is on the order of 20% within each one of the two methods.

In a previous determination of the specific surface area of a sample of single-walled carbon nanotubes using a variety of spherical adsorbates (neon, argon, methane, and xenon), we found essentially the same value for this quantity regardless of the size of the adsorbate used.³⁰ In that study, the point B method was employed to determine monolayer capacity of the HiPco single-walled carbon nanotube sample. The result for spherical adsorbates stand in stark contrast with our present finding for the sequence of alkanes, from methane to butane, presented in this article. The main difference is that the adsorbates on which we are reporting here are not spherical but linear (this results in an enhancement of the multisite occupancy nature of their adsorption behavior).

RRR Approach. As stated, in the 1-D case, the RRR method coincides with the BET equation for monomers, $k = 1$ (see ref 8). The exact form arrived at for the case of dimers ($k = 2$) in 1-D in the RRR approach is given by

$$n = \frac{n_m}{1-P/P_0} \left\{ 1 - \left[\frac{1-P/P_0}{1+(4C-1)P/P_0} \right]^{1/2} \right\} \quad (2)$$

The quantities in eq 2 mean the same as they do in eq 1.

Equation 2 can be used to calculate the monolayer capacity and the specific surface area in the case for ethane molecules (which can well be treated as dimers). Unlike the case for the BET equation, the RRR dimer equation is not linear. For ethane, the value for the area obtained using eq 2 is greater than that determined from the application of the BET equation to the same data. Interestingly for this case, there are just two adjustable parameters in the RRR approach, the same number as there are for the BET equation.

As was already noted, no exact solutions exist for adsorption isotherms (i.e., for the specification of the fractional coverage, n , as a function of P/P_0) for the 2-D case, for $k > 1$. In order to deal with this problem, we took two different approaches to obtain the monolayer capacity from the experimental data:

(1) In the first approach (procedure A), in order to include the effects of the linear nature of the adsorbate, we used 1-D RRR expressions for all four adsorbates. Specifically, we used the BET equation for methane (this is equivalent to the RRR approach for monomers); we used the exact 1-D expression derived in the RRR approach for the case of dimers (eq 2) for ethane, and for propane and butane, we fitted the parameters used in the RRR exact 1-D expression for dimers to the data for propane and butane in the low-coverage, low-pressure regime (i.e., over the same region that is used for the BET equation).

When procedure A is used, there is an increase in the value of the specific area determined with ethane, propane, and butane

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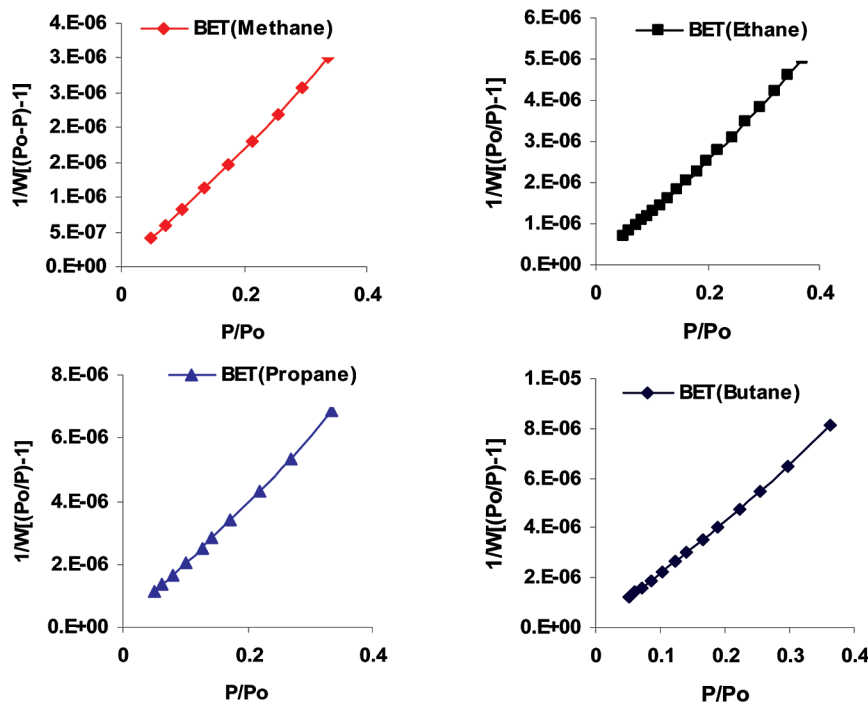


Figure 3. BET analysis for the adsorption isotherms for methane, ethane, propane, and butane on single-walled carbon nanotubes shown in Figure 2.

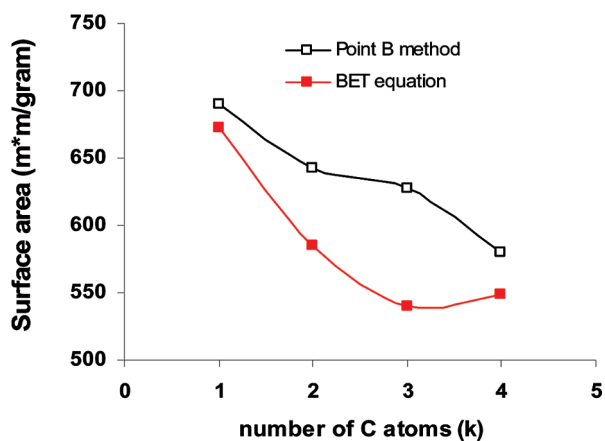


Figure 4. Specific surface area of single-walled carbon nanotubes computed using the BET and the point B methods. The specific surface area in m^2/g (Y axis) is presented as a function of number of carbon atoms in the adsorbate (X axis).

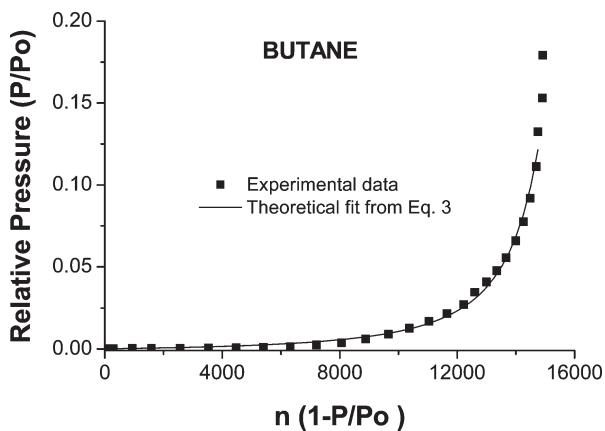


Figure 5. Fit of the low-pressure region of the butane isotherm data to eq 3 in the text (obtained in the RRR approach). The value of the monolayer capacity is extracted from this fit.

relative to the specific surface areas determined when the same data is analyzed with the BET equation.

In addition to yielding better values than the BET equation applied to the same data, this method has the advantage of being simple to use.

We note, however, that also in this case there is a clear tendency toward lower specific surface area values as a function of increasing alkane length (see Figure 6, which displays these data as well as others).

The results of procedure A, although not ideal, represent an improvement over the BET method.

(2) The second approach that we used (procedure B) was to fit the data for all four adsorbate species to the approximate expression arrived at in the RRR approach for the 2-D case (eq 31 in ref 8):

$$P/P_0 = \frac{\frac{n(1-P/P_0)}{n_m} \left\{ 1 - \frac{k-1}{k} \left[\frac{n(1-P/P_0)}{n_m} \right]^{k-1} \right\}}{k C_{ef} \left[1 - \frac{n(1-P/P_0)}{n_m} \right]^k + \frac{n(1-P/P_0)}{n_m} \left\{ 1 - \frac{k-1}{k} \left[\frac{n(1-P/P_0)}{n_m} \right]^{k-1} \right\}} \quad (3)$$

Here C_{ef} is a constant that depends on the adsorbate–substrate interaction and the lattice connectivity, and k is the number of “mers” in the k -mer.

The experimental adsorption isotherm data are fitted to this expression, with the appropriate value of k (1, 2, 3, or 4 depending on the adsorbate), over the same low-pressure range that is used in the fits to the BET equation. The results of this fit for butane are presented in Figure 5 (similarly good fits are obtained for the case of the other three adsorbates). The fits give values for the monolayer completion, n_m , which are then used in the calculation of the specific surface area.

In Figure 6 we present our main results. This figure displays the specific surface areas for the substrate computed according to the four methods discussed (point B, BET equation, 1-D

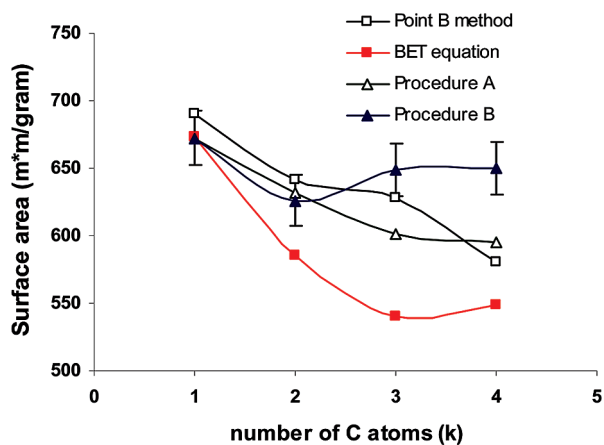


Figure 6. Computation of the specific surface area of single-walled carbon nanotubes using BET, point B, procedure A, and procedure B methods. The specific surface area in m^2/g (Y axis) is presented as a function of number of carbon atoms in the adsorbate (X axis). (Error bars are only used for procedure B in order not to clutter unnecessarily this figure.)

RRR equation, and 2-D RRR equation), plotted as a function of the number of C atoms present in the alkanes used in the adsorption isotherms. We note that of these four only the 2-D RRR equation approach (procedure B) yields values for the specific surface area that are nearly constant. The other three approaches, to varying degrees, yield surface areas that decrease with increasing adsorbate chain length.

The practical relevance of this result is that it provides a means for determining consistently the surface area of a substrate when different linear adsorbates are used. That is, with this method we can obtain with linear molecules a behavior that is analogous to that obtained when the BET or the point B method are used with spherical adsorbates.

From a more fundamental perspective, our results highlight the importance of the additional entropy term that arises in the monolayer film of linear molecules as a result of multisite occupancy.

V. Conclusions

We have conducted adsorption isotherm measurements with a sequence of four alkanes ($n = 1$ to $n = 4$). We have used these results to calculate the specific surface area of the same substrate using four different approaches: the more traditional BET equation and point B method as well as two approaches (a 1-D and 2-D versions) using a newer model for the adsorption isotherm of linear molecules, the RRR method. Our main conclusion is that the 2-D RRR approach (procedure B) provides a consistent value for the area of the substrate when this quantity is measured using various linear adsorbates. This is not the case with other approaches studied here (point B, BET equation, or 1-D RRR approach).

This result is important from both a practical and a fundamental perspective. It provides a method of obtaining values for the specific surface area using longer linear molecules, which yields values for the specific surface area that are consistent with those determined using spherical adsorbates and the BET equation. This facilitates comparisons of different results on the same type of substrate.

From a fundamental perspective, the result illustrates the importance of considering the entropic effects associated with excluded spaces on a substrate when dealing with linear adsorbates.

Our data and theoretical comparisons also help point out explicitly one of the weaknesses of the BET approach, namely, the fact that its applicability is limited to monomers.

Acknowledgment. A. D. Migone acknowledges support provided for this study by National Science Foundation through Grant DMR-0705077. A. J. Ramirez-Pastor acknowledges support from the CONICET (Argentina) through Project PIP 112-200801-01332 and the National Agency of Scientific and Technological Promotion (Argentina) under Project 33328 PICT 2005.