Lawrence Berkeley National Laboratory
Recent Work

Title
Donnan Equilibrium: Hypernetted-Chain Study of One- and Multicomponent Models for Aqueous Polyelectrolyte Solutions

Permalink
https://escholarship.org/uc/item/9jr2s9tt

Journal
Journal of physical chemistry, 96(15)

Authors
Vlachy, V.
Prausnitz, John M.

Publication Date
1992-02-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Donnan Equilibrium: Hypernetted-Chain Study of One- and Multicomponent Models for Aqueous Polyelectrolyte Solutions

V. Vlachy and J.M. Prausnitz

February 1992

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Donnan Equilibrium. Hypernetted-Chain Study
of One- and Multicomponent Models for Aqueous
Polyelectrolyte Solutions

V. Vlachy [a] *and J. M. Prausnitz* [b]

Department of Chemical Engineering

University of California

and

Chemical Sciences Division

Lawrence Berkeley Laboratory

1 Cyclotron Road

Berkeley, CA 94720

[a] On leave from the Department of Chemistry, University of Ljubljana, Ljubljana, Slovenia.

[b] To whom correspondence may be addressed.

ABSTRACT

The hypernetted-chain integral equation has been applied to two polyelectrolyte models to study the Donnan equilibrium for an aqueous mixture containing large polyions and ordinary ionized salts. The first is a traditional one-component model with the polyions interacting via a screened Coulomb potential. The second is a multicomponent model which describes the solution as an aqueous mixture of a highly asymmetric electrolyte where polyions, counterions and coions are represented by charged hard spheres. The polyion-polyion distribution functions and the Donnan pressure are evaluated for a range of typical experimental conditions for aqueous solutions of globular proteins. The results show that a screened Coulomb potential model provides a good approximation if the charge on the polyions is not too high. However, there are some important differences between the results of one- and multicomponent models for the polyion-polyion distribution function. At concentrations above 1 M of simple electrolyte, there is a region of interparticle distances for which the potential of mean force is attractive according to the multicomponent model; while this effect is not reproduced by the one-component model based on the screened Coulomb potential alone, it is shown correctly when we include an "osmotic" potential due to the presence of the small ions. Using the hypernetted-chain theory, a one-component model provides a successful analysis of experimental osmotic-pressure data of aqueous solutions of bovine serum albumin in 0.15 M sodium chloride for albumin concentrations up to 450 g/l.

INTRODUCTION

Toward increasing theoretical understanding of the
properties of aqueous polyelectrolytes, this work considers the
Donnan equilibrium [1-3] which is established by the
equilibrium distribution of a simple electrolyte between an
aqueous polyelectrolyte-electrolyte solution and an aqueous
solution of the same simple electrolyte, when the two phases
are separated by a semipermeable membrane. A difference in
osmotic pressures exists across a membrane impermeable for
polyions; this difference can be measured, providing important
information about solute-solute interactions in polyelectrolyte
solutions.

Traditionally, osmotic-pressure measurements have been
applied to dilute solutions to obtain molecular weight and
conformational data. Application is usually limited to dilute
systems because there is little familiarity with a quantitative
theory able to explain the behavior of highly nonideal systems.
An earlier theoretical treatment of Donnan equilibrium was given
by Hill [4,5]. Recently, Stell and coworkers have successfully
applied techniques of modern statistical mechanics to this
problem [6-9].

The properties of solutions of colloids, micelles and
globular proteins are often dominated by Coulombic interactions
between highly charged polyions and small ions. There are at
least three levels of theoretical description which may be used
to study polyelectrolyte solutions. The first is the so-called
cell model [10], which is motivated by the asymmetry in size
and magnitude of charge between the species. The second level,
providing the most widely used model, describes the solution as

an effective one-component fluid with electrostatic interactions modeled by a screened Coulomb potential [11]. The effects of a solvent and a dissolved simple electrolyte are given in the continuum approximation; only the polyion-polyion interactions are considered explicitly. In the third level, here called the multicomponent model, the solution is described as a mixture of charged hard spheres, while the solvent is still considered to be a continuum [12]. This multicomponent model is an extension of the so-called "primitive model" of simple electrolyte solutions.

Solutions of asymmetric electrolytes have recently been studied by computer simulations and integral equations [13-16]. One of them, the hypernetted- chain integral (HNC) equation, provides physically meaningful agreement with the Monte-Carlo data. When applied to multicomponent models, the HNC theory is computationally very demanding and therefore not appealing for analysis of experimental data; one-component model HNC calculations require much less computational effort [17]. Because so many experimental data exist in the form of the polyion-polyion structure factor, $S_{pp}(k)$, the one-component approach is popular. The preferred one-component model, based on the McMillan-Mayer theory [5,18], yields in a natural way the Donnan pressure, an experimentally well-studied property. The goal of this work is to examine the importance of simplifying assumptions inherent in the one-component model.

Several authors have analyzed the approximations in the one-component model which uses a screened Coulomb interaction between polyions [16,19-21]. In this paper we present a numerical study of both the one-component and the multicomponent models, using the same statistical-mechanical theory. The HNC integral equation is applied to both models of polyelectrolyte solutions to obtain results for thermodynamic

and structural properties. In particular, the Donnan pressure is studied for a range of polyelectrolyte and electrolyte concentrations and for a range of charges on the polyion. The data are used to test the validity of the one-component model (or screened Coulomb potential) over a range of parameters, mimicking typical experimental conditions for solutions of globular proteins. The objective of this work is to establish the simplest meaningful molecular model of polyelectrolyte solutions to facilitate significant interpretation of experimental data for aqueous solutions of globular proteins.

POLYELECTROLYTE MODELS

a) Potential for the one-component model

Here, the solution is modeled as a solution of single-component macroparticles with diameter σ, interacting through the screened Coulomb potential in the form [11]

$$\beta u_R(r) = A/r \exp [-\kappa r], \qquad r > \sigma,$$
$$\beta u_R(r) = \infty, \qquad r < \sigma, \qquad (1)$$
$$A = z_P^2 L_B \exp(\kappa\sigma)/(1 + \kappa\sigma/2)^2, \qquad \text{and}$$
$$L_B = \beta e^2/(4\pi\epsilon_0\epsilon_r).$$

In Equation (1), r is the distance between macroion centers, $z_P e$ is the charge on a polyion and, as usual, $\beta^{-1} = k_B T$ (T is the absolute temperature and k_B Boltzmann's constant). The solvent and simple ions are not treated explicitly; they are reflected

in the screening length κ^{-1} and in the relative permittivity ϵ_r of the solution. Equation (1) gives the free energy of bringing two macroions isothermally from $r=\infty$ to $r=r$ in a solution containing "ordinary" ions such that the screening (Debye) length is κ^{-1}. When the macroions are at infinite dilution, Equation (1) gives the potential of mean force.

An attractive van der Waals term can be added to the top line of Equation (1) to account for short-range attraction between the macroparticles.

b) Potential for the multicomponent model

In this model all ions are represented as charged hard spheres, immersed in a continuous dielectric representing the solvent [12]. The potential energy between ions i and j, $u_{ij}(r)$, is

$$u_{ij}(r) = z_i z_j e^2 / (4\pi\epsilon_0\epsilon_r r) \quad , \ r > \sigma_{ij}$$
$$u_{ij}(r) = \infty \qquad\qquad , \ r < \sigma_{ij}, \qquad\qquad (2)$$

where $z_i e$ is the charge on ionic species i, and $\sigma_{ij}=(\sigma_i+\sigma_j)/2$. The solution is modeled as a mixture of charged hard spheres.

THE HNC INTEGRAL EQUATION

Integral-equation theories are based on the diagrammatic

expansion of the total correlation function h(r)=g(r)-1, where g(r) is the radial distribution function. For a mixture, the total correlation function $h_{ij}(r)$ may be written as [18]

$$h_{ij}(r) = \exp[-\beta u_{ij}(r) + E_{ij}(r) + h_{ij}(r) - c_{ij}(r)] - 1, \qquad (3)$$

where $E_{ij}(r)$ is the so-called bridge function and $c_{ij}(r)$ is the direct correlation function defined via the Ornstein-Zernike equation [18]

$$h_{ij}(r_{ij}) = c(r_{ij}) + \Sigma_k \rho_k \int dr_k c_{ik}(r_{ik})h_{kj}(r_{kj}), \qquad (4)$$

where ρ_k stands for the number density of component k. In general, the bridge function $E_{ij}(r)$ is unknown and the HNC approximation sets $E_{ij}(r)=0$. For a "three-component" system (polyions, counterions and coions) there are six total correlation functions and the same number of direct correlation functions. Altogether a system of six coupled integral equations has to be solved numerically.

To avoid divergence of integrals with potentials proportional to r^{-1}, the long-range (Coulombic) interactions require special treatment. The pair potential $u_{ij}(r)$ may be separated into a short-range part (s) and a long-range Coulombic part (1), $u^1_{ij}(r)$. The long-range part of the direct correlation function, given by $c^1_{ij}(r)=-\beta u^1_{ij}(r)$ [18], is subtracted from $c_{ij}(r)$ to yield $c^s_{ij}(r)$, a well-behaved function of shorter range. Details of the numerical procedure to solve the multicomponent HNC equation have been described in several recent papers [13,14,22] and need not be repeated here. The computer program, previously used for single electrolytes [13,14], is extended to apply to solutions with more than two species of ions [23].

An application of the HNC equation to a one-component model (Equation 1) requires a computational effort which is at least an order of magnitude smaller than that for the multicomponent case [17].

THE DONNAN PRESSURE

Once results for the radial distribution functions are known, the thermodynamic properties may be determined using standard equations [18]. In particular, the equation of state has been evaluated via the so-called "virial" route [18]. For the multicomponent model we obtain:

$$\beta \frac{P}{\rho} = 1 - \frac{\beta}{6\rho} \sum \sum \rho_i \rho_j \int r \left(\frac{\partial u_{ij}}{\partial r} \right) g_{ij}(r) 4\pi r^2 dr \qquad (5)$$

where $\rho = \Sigma \rho_i$. Within the McMillan-Mayer framework, P is the osmotic pressure of the solution at temperature T and solute number concentrations ρ_i. The procedure to evaluate the Donnan pressure for the multicomponent model is described below.

Chemical equilibrium across a membrane requires that for each permeable charged species, the electro-chemical potential is the same in both compartments. Chemical equilibrium also requires the equality of the chemical potential of water on both sides. We denote the osmotic pressure in the polyelectrolyte-electrolyte mixture as P^β and the osmotic pressure in "ordinary" electrolyte solution as P^α. Similarly, the ionic activities on both sides are defined as a_i^β and a_i^α.

The Donnan pressure Π is defined as $\Pi = P^\beta - P^\alpha$. Under conditions of interest for us ($\Pi < 5\times10^5$ Pa), the activities of water on both sides do not differ appreciably [24] and for the 1:1 electrolyte added to a polyelectrolyte solution we obtain

$$a_+^\beta a_-^\beta = a_-^\alpha a_+^\alpha = a_{\pm,s}^2 ,$$

(6)

In Equation (6) $a_{\pm,s}$ is the mean activity of pure electrolyte at molar concentration n_s. To evaluate Π we must first solve the HNC equation for a polyelectrolyte-electrolyte mixture to obtain the osmotic pressure P^β [Equation (5)] and ionic activities, a_+^β and a_-^β. Once the activities of small ions in a polyelectrolyte-electrolyte mixture are known, the HNC equation is used again to determine the equilibrium concentration n_s and the osmotic pressure P^α of "ordinary" electrolyte with mean activity $a_{\pm,s}$ [cf. Equation (6)]. This, however, can only be done by a trial-and-error procedure. The activity coefficients $\gamma_i = a_i/n_i$ are obtained in the framework of the HNC approximation [12]:

(7)

$$\ln\gamma_i = \sum_j \{-\rho_j \hat{c}_{ij}^s(0) + 2\pi\rho_j \int h_{ij}(r)\,[h_{ij}(r) - c_{ij}(r)]\,r^2\;dr \}$$

where $c_{ij}^s(r)$ is the short-range part of the direct correlation function and the caret denotes the Fourier transform. Equation (7) provides only an approximation whose accuracy has not as yet been thoroughly tested.

Finally, the Donnan pressure is evaluated as a difference

between two osmotic pressures, $\Pi = P^\beta - P^\alpha$. The numerical error associated with this procedure (frequently $P^\alpha \approx P^\beta \gg \Pi$) is given in Table 1 and indicated in Figure 2. For a one-component model, the Donnan pressure can be obtained directly using the one-component version of Equation (5).

THEORETICAL RESULTS

a) The Donnan potential: Comparison with Monte-Carlo data

The Donnan potential Ψ is defined by $\beta e\Psi = \ln(a_i^\beta/a_i^\alpha)$. Recently, limited Monte-Carlo results for the Donnan potential have become available [25]. Figure 1 compares the HNC results with Monte-Carlo data for the same (multicomponent) model, as a function of polyion charge $z_p e$. For salt-free polyelectrolyte systems, it was found previously [13-16] that the Monte-Carlo method and the HNC equation are in reasonable, but not exact, agreement. The same conclusion can be inferred from the limited comparison presented in Figure 1. Unfortunately, the HNC approximation does not yield a convergent solution for highly charged systems; therefore we have not been able to obtain results for $|z_p|=35$ and higher. Zhou and Stell [9] have studied the Donnan potential by using various integral-equation theories. As shown in Figure 2 of Reference 25, their "best theory" is in equally good or even slightly better agreement with the simulation data than our HNC result.

b) The Donnan pressure

Figure 2 and Table 1 present a comparison between results
for the Donnan pressure Π as obtained by various models. Figure
2 shows the Donnan pressure as a function of polyion charge
$z_P e$. The radius of polyion in this calculation is 2.0 nm, and
the distance of closest approach between small ions is 0.4 nm.
All results apply to aqueous solutions at 298 K. The
concentration of counterions (n_+) in polyelectrolyte-
electrolyte mixtures is 0.1 M, and therefore $n_- = n_+ - |z_P| n_p$.
As indicated in Figure 2, agreement between the two models is
good, except for highly charged polyelectrolytes with $|z_P| >$
25. We cannot now say which of these calculations is more
accurate because the HNC approximation becomes less reliable
when applied to highly charged asymmetric electrolytes [13-
15]. To answer this question we need to evaluate the leading
term in the bridge function $E_{ij}(r)$ [Equation (3)], as proposed
in Reference 14.

Table 1 presents additional results for the Donnan
pressure. As expected, good agreement is obtained for a
relatively low charge on the protein and for systems where a
simple electrolyte is added in excess. The electrostatic
interactions in these systems are suppressed to the degree that
there is little difference in the activity coefficients of the
simple electrolyte on both sides of the membrane. In other
words, the system behaves as an ideal Donnan system. Good
agreement between the two levels of description applies to the
concentration range (cases 3 and 5 in Table 1; cf. also Figures
1 and 4a) where a simple electrolyte is added in only moderate
excess. This corroborates the findings of Linse [16] for the
two-component model, i.e. for salt-free polyelectrolyte
solutions. His conclusion is that the screened Coulomb
potential yields an accurate description of the structure in

solutions of polyions and counterions.

c)   The polyion-polyion distribution function

One aim of this work is to contribute toward better understanding of the role of electrostatic interactions in solutions of globular proteins with the ultimate goal to develop a predictive theory for protein precipitation. In this respect, it is important to consider the difference between the two levels of description shown in Figure 3. In this figure the value of the polyion-polyion distribution function at contact, $g_{pp}(a)$, is plotted as a function of the concentration of simple electrolyte, n (n=n_) in a polyelectrolyte-electrolyte mixture. While the distribution function, obtained by the screened Coulomb model, is always smaller than unity, the $g_{pp}(a)$ as obtained by the multicomponent model increases above unity for salt concentrations higher than 1 M. In other words, the probability of finding two polyions next to each other (in the multicomponent model) increases strongly with the concentration of simple electrolyte, and it is substantially underestimated by the one-component model described above. This increase represents an essential driving force for protein precipitation [26-28]. We discuss this important question below.

Figure 4 presents the polyion-polyion distribution functions as obtained by two models. Figure 4a shows $g_{pp}(r)$ for polyions with z_P=-20 at electrolyte concentration n=0.04 M, and n_p=0.002 M. For this case, the distribution functions obtained by different models are in very good agreement. On the other hand, correlation functions presented in Figure 4b (z_p=-6, n=1.5 M, and n_p=0.0005 M) are in total disagreement.

There is a region of interparticle distances r, for which the potential of mean force is attractive according to the multicomponent model. This effect, however, is not reproduced within the one-component level that was used here. It is evident that something is missing from our one-component model.

The difference between the two models in describing the polyion-polyion distribution function at high salt concentrations stems from the osmotic pressure due to the small mobile ions on a pair of closely adjacent polyions [19,27-29]. Under certain conditions, this attractive contribution may overshadow the repulsion between two polyions. This interaction is missing in the one-component level of description, where the ions have no size and enter into the pair potential only via the screening length. The effect vanishes for more strongly charged polyions ($|z_P|>18$) and seems not to be an artifact of the HNC equation [30].

To illustrate this osmotic effect, the potential of mean force for the one-component model, Equation (1), has been corrected to include the "osmotic" attraction potential of Asakura and Oosawa [27] used also by Hall et al. [28].

$$
\begin{aligned}
u(r) &= \infty, & r<\sigma_2, \\
u(r) &= u_R(r)-4\pi\beta^{-1}\sigma_{23}{}^3\rho_3/3 \ [1-3r/4\sigma_{23}+r^3/16\sigma_{23}{}^3], & \sigma_2<r<2\sigma_{23}, \quad (8) \\
u(r) &= u_R(r), & r>2\sigma_{23}.
\end{aligned}
$$

In Equation (8) σ_2 is the diameter of the polyion, σ_3 is the diameter of the small ion (0.4 nm for this calculation), ρ_3 is the number concentration of small ions and $\sigma_{23}=(\sigma_2 + \sigma_3)/2$. Equation (1) gives $u_R(r)$. The results for the corrected one-component potential given by Equation (8) are presented in Figure 4b (filled triangles). These results show an essential improvement over the previous calculation (continuous line in

Figure 4b), based on Equation (1) alone. Inclusion of the attractive potential described by Equation (8) gives a significant contribution only for high concentrations of simple electrolyte (above 1 M) and does not affect the excellent agreement between the one- and multicomponent models presented in Figure 4a.

COMPARISON WITH EXPERIMENTAL OSMOTIC-PRESSURE DATA

The calculations presented above indicate that there is a range of experimental parameters for which the screened Coulomb potential correctly reproduces the results of the more realistic multicomponent model. This is helpful since the one-component model is numerically much easier to implement. In this final section we apply the HNC integral equation to a one-component model to analyze the experimental data of Vilker, Colton and Smith [31]; they report Donnan-pressure measurements of bovine serum albumin (BSA) solutions for concentrations ranging from 84 to 475 g/l in 0.15 M sodium chloride at several pH. The charge on the protein as a function of pH has also been determined. The authors have based their analysis on the classical one-component model (DLVO), where the pair potential u(r) between two proteins is given by [11]:

$$u(r) = u_A(r) + u_R(r), \qquad\qquad (9)$$

and $u_R(r)$, the repulsive part of the potential, is described by

Equation (1). The attractive part of the potential, representing dispersion interactions, is [11]:

$$u_A(r) = -\frac{H}{12}[\frac{1}{s^2} + \frac{1}{(s^2-1)} + 2\ln(1-\frac{1}{s^2})] \quad (10)$$

where H is the Hamaker constant and s=r/σ. Other contributions to the potential of mean force are considered to be less important under these conditions; they are not included in their or our calculations [31]. The contribution of "osmotic" forces [Equation (8)] is negligible because ρ_3 is very small for the conditions considered here.

The theoretical analysis presented in Reference 31 is based on the virial expansion, derived by McMillan and Mayer [5,18,32].

$$P = RT\ [\frac{n_2}{M_2} + B_{22}n_2^2 + B_{222}n_2^3 + ..] \quad (11)$$

In Equation 11, R is the universal gas constant, n_2 is the protein concentration in g/l, B_{22} is the second and B_{222} the third virial coefficient. From the potential of mean force, given by Equation (9), the second and the third virial coefficients have been calculated. The fourth and fifth virial coefficients have been approximated by the corresponding terms for a solution of hard spheres. Agreement between theory and experiment, presented in Figure 10 of Reference 31, is poor. The predicted curves fail to show the experimentally observed sensitivity of osmotic pressure to solution pH, i.e. to the protein charge. This failure has led Vilker et. al. [31] to

the conclusion that the major defect in the analysis is in the description of the potential of mean force.

In what follows we show that the potential of mean force, given by Equation (9), may yield reasonable agreement with the experimental data, provided that a more accurate statistical-mechanical theory is used. In this analysis we use the same potential function [Equations (9) and (10)] and exactly the same values of parameters as those used previously by Vilker et. al. [31]. The only difference between the two calculations is that we apply the HNC integral equation to evaluate the Donnan pressure instead of a truncated virial expansion. In Reference 17, the HNC equation applied to the screened Coulomb model [Equation (1)] has been tested against the Monte-Carlo data. The conclusion is that the theory yields reliable predictions for thermodynamic variables, except for highly structured fluids close to the order-disorder transition, where a better approximation for the bridge graph has to be used [17,25].

Figures 5 and 6 compare results for the Donnan pressure as obtained by the HNC equation with the experimental data [31]. The comparison applies to pH=7.4 and 5.4 where the average number of (negative) charges on the BSA is 20.4 and 9.2, respectively. The protein radius is 3.13 nm and the Hamaker constant H is 1.65×10^{-21} J [31]. Agreement between experiment and theory is now satisfactory. It is especially gratifying that the simple model given by Equation (9) reproduces well the pH dependence observed experimentally.

We do not show a comparison for the Donnan pressure at pH=4.5 where the average number of charges on the BSA is about 4.5. For this case, the agreement between HNC theory and experiment, though better than that obtained before [31], is

merely qualitative. As pointed out by Vilker et. al. [31], poor agreement is due to the approximations in Equation (9) [33]. For example, the model used here (and in Reference 31) is not able to take into account lowering of the osmotic pressure due to the formation of dimers or higher oligomers. This effect is more important for pH=4.5 where the charge on the protein is low.

CONCLUSIONS

In their analysis, Medina-Noyola and McQuarrie [19] have pointed out basic approximations in the derivation of the screened Coulomb potential as a substitute for a more realistic multicomponent description of polyelectrolyte solutions. Our calculations based on the HNC integral equation show that these approximations may not be severe for the range of parameters describing globular proteins. This means that a one-component model with a DLVO potential [11] may be used as a starting point to describe phase separation in globular proteins, induced by a simple electrolyte. At higher salt concentrations the DLVO potential must be modified to include an attractive "osmotic" contribution [27]. Our calculations, based on the one-component (DLVO) model and the HNC theory, yield good agreement with experimental data for the Donnan pressure. These results also demonstrate that, unless an accurate statistical-mechanical theory is used, conclusions concerning suitability of a physical picture may be misleading.

REFERENCES

1) J.W. Gibbs, Collected Papers, Vol.II (Yale University,New Haven,1948).

2) F. Donnan, Z. Electrochemie **17**,572(1911).

3) J.Th.G. Overbeek, Prog. Biophys. Biophys. Chem. **6**,57(1956).

4) T.L. Hill, J. Am. Chem. Soc. **80**,2923(1958).

5) T.L. Hill, Introduction to Statistical Mechanics (Addison-Wesley,Reading,1960).

6) V. Romero-Rochin, E. Martina, and G. Stell, Molec. Phys. **52**,1047(1984).

7) G. Stell and C.G. Joslin, Biophs. J. **50**,855(1986).

8) Y. Zhou and G. Stell, J. Chem. Phys. **89**,7010(1988).

9) Y. Zhou and G. Stell, J. Chem. Phys. **89**,7020(1988).

10) D. Bratko and V. Vlachy, Colloid&Polymer Sci. **263**,417(1985).

11) E.J.W. Verwey and J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids (Elsevier,Amsterdam,1948).

12) L. Belloni, Chem. Phys. **99**,43(1985).

13) V. Vlachy, C.H. Marshall, and A.D.J. Haymet, J. Am. Chem. Soc. **111**,4160(1989).

14) J. Reščič, V. Vlachy, and A.D.J. Haymet, J. Am. Chem. Soc. **112**,3398(1990).

15) P. Linse, J. Chem. Phys. **93**,1376(1990).

16) P. Linse, J. Chem. Phys. **94**,3817(1991).

17) V. Vlachy, C. Pohar, and A.D.J. Haymet, J. Chem. Phys. **88**,2066(1988).

18) H.L. Friedman, A Course in Statistical Mechanics (Prentice Hall,Englewood Cliffs,NJ,1985).

19) M. Medina-Noyola and D.A. McQuarrie, J. Chem. Phys. **73**,6279(1980).

20) L. Belloni, J. Chem. Phys. **85**,519(1986).

21) C.E. Woodward and B. Jonsson, J. Phys. Chem. **92**,2000(1988).

22) T. Ichiye and A.D.J. Haymet, J. Chem. Phys. **89**,4315(1988).

23) M. Bešter and V. Vlachy, J. Chem. Phys., in press (1992).

24) E.A. Guggenheim, Thermodynamics (North Holland, Amsterdam, 1950).

25) B. Svensson, T. Akesson, and C.E. Woodward, J. Chem. Phys. **95**, 2717 (1991).

26) P.D. Patel and W.B. Russel, J. Colloid Interface Sci. **131**, 192 (1989).

27) S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954).

28) H. Mahadevan and C.K. Hall, AIChE J. **36**, 1517 (1990), and references therein.

29) P. Attard and G.N. Patey, J. Chem. Phys. **92**, 4970 (1990).

30) M. Teubner, J. Chem. Phys. **75**, 1907 (1981).

31) V.L. Vilker, C.L. Colton, and K.A. Smith, J. Colloid Interface Sci. **79**, 548 (1981).

32) W.G. McMillan and J.E. Mayer, J. Chem. Phys **13**, 276 (1945).

33) K. Tamura, C.A. Haynes, H.R. Körfer, H.W. Blanch, and J.M. Prausnitz, J. Phys. Chem., in press (1992).

TABLE 1. Π_1 and Π_m are Donnan pressures for the one- and multicomponent model, respectively, in Pascal units and n is the concentration of electrolyte (n=n_) in the polyelectrolyte-electrolyte mixture. The polyion radius is 2.0 nm and the small-ion radius is 0.2 nm. Uncertainties in Π_1 are about 1-2%.

$n_p 10^3/M$	$-z_P$	n/M	Π_1/Pa	Π_m/Pa
1. 0.1	10	0.99	249	250 ± 10
2. 1.0	10	0.09	2946	3025 ± 60
3. 5.0	10	0.05	33530	35350 ± 400
4. 0.5	12	0.25	1304	1310 ± 20
5. 2.0	20	0.04	12300	11200 ± 200

Figure Captions

Figure 1. The reduced Donnan potential, $\beta\Psi e$, as a function of macroionic charge. Symbols are Monte-Carlo data as compiled from Figure 2 of Reference 25, and the line represents HNC results for the multicomponent model. Polyelectrolyte concentration is 0.001 M, small ions have radii 0.2 nm and the polyion radius is 2.0 nm. The concentration of counterions in the polyelectrolyte-electrolyte mixture n_+ is 0.1 M. The relative permittivity of the solution is 78.5.

Figure 2. The Donnan pressure as obtained by the HNC-integral-equation theory for the one-component (line) and multicomponent model (symbols) as a function of $-z_P$. Data as in Figure 1.

Figure 3. The polyion-polyion correlation function at contact, as obtained for the one-component model (line) and the multicomponent model (symbols) as a function of the concentration of simple electrolyte n. In this calculation $z_P=-12$ and $n_p=0.0005$ M.

Figure 4. The polyion-polyion correlation functions as a function of r. Squares denote results for the multicomponent model and the lines show results for the screened Coulomb model [Equation (1)]. Figure 4a: $-z_P=20$, n=0.04 M, and $n_p=0.002$ M, Figure 4b: $-z_P=6$, n=1.5 M and $n_p=0.0005$ M. Filled triangles show results for the one-component model augmented by Equation (8).

Figure 5. The reduced Donnan pressure Π/n_2 as a function of the protein (BSA) concentration n_2 for pH=7.4 ($-z_P=20.4$). Donnan pressure is in mm Hg; n_2 in g/l. Symbols denote experimental data [31] and the line represents HNC calculations.

Figure 6. The reduced Donnan pressure Π/n_2 as a function of protein (BSA) concentration n_2 for pH=5.4 ($-z_P=9.2$). Symbols as for Figure 5.
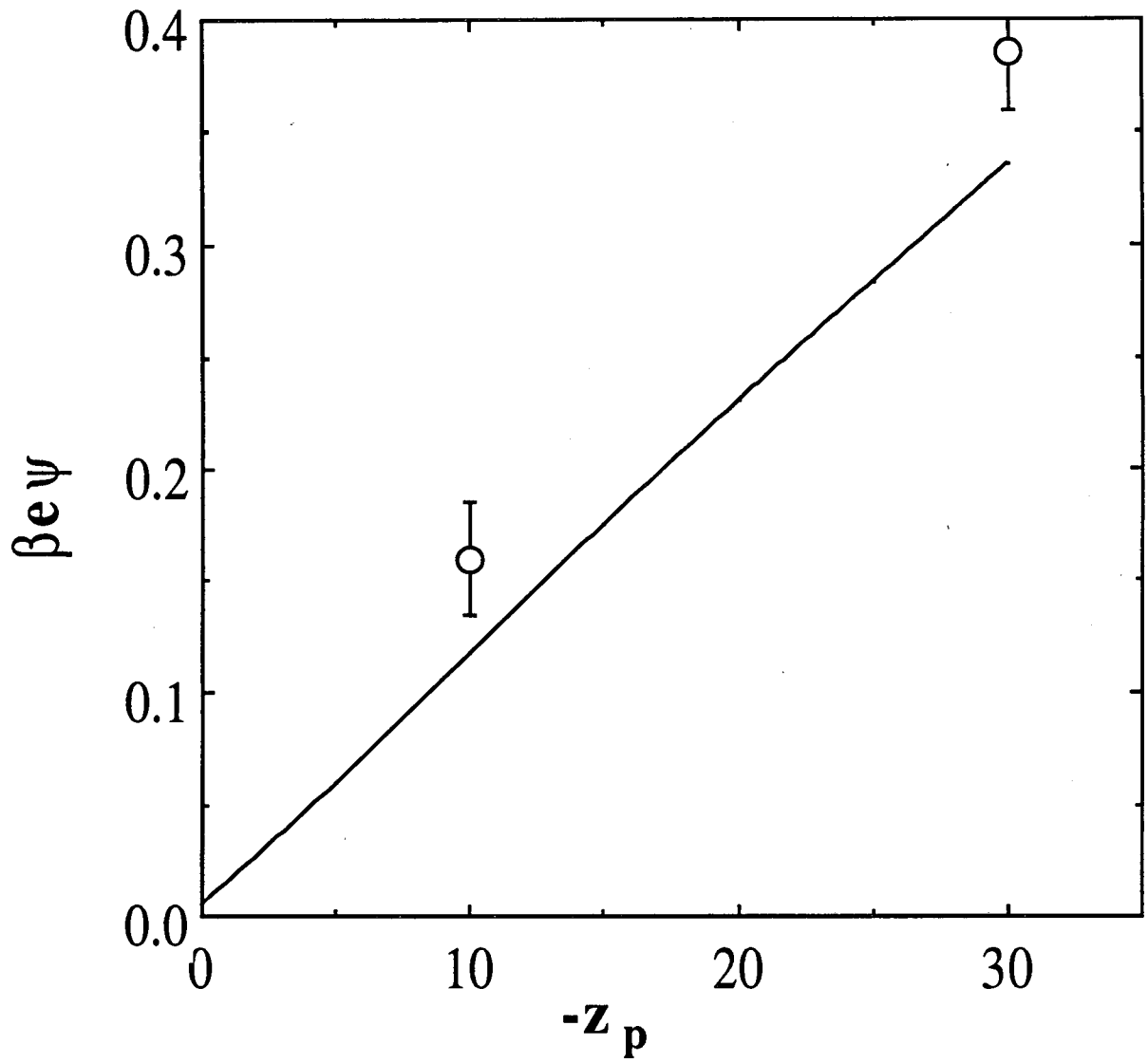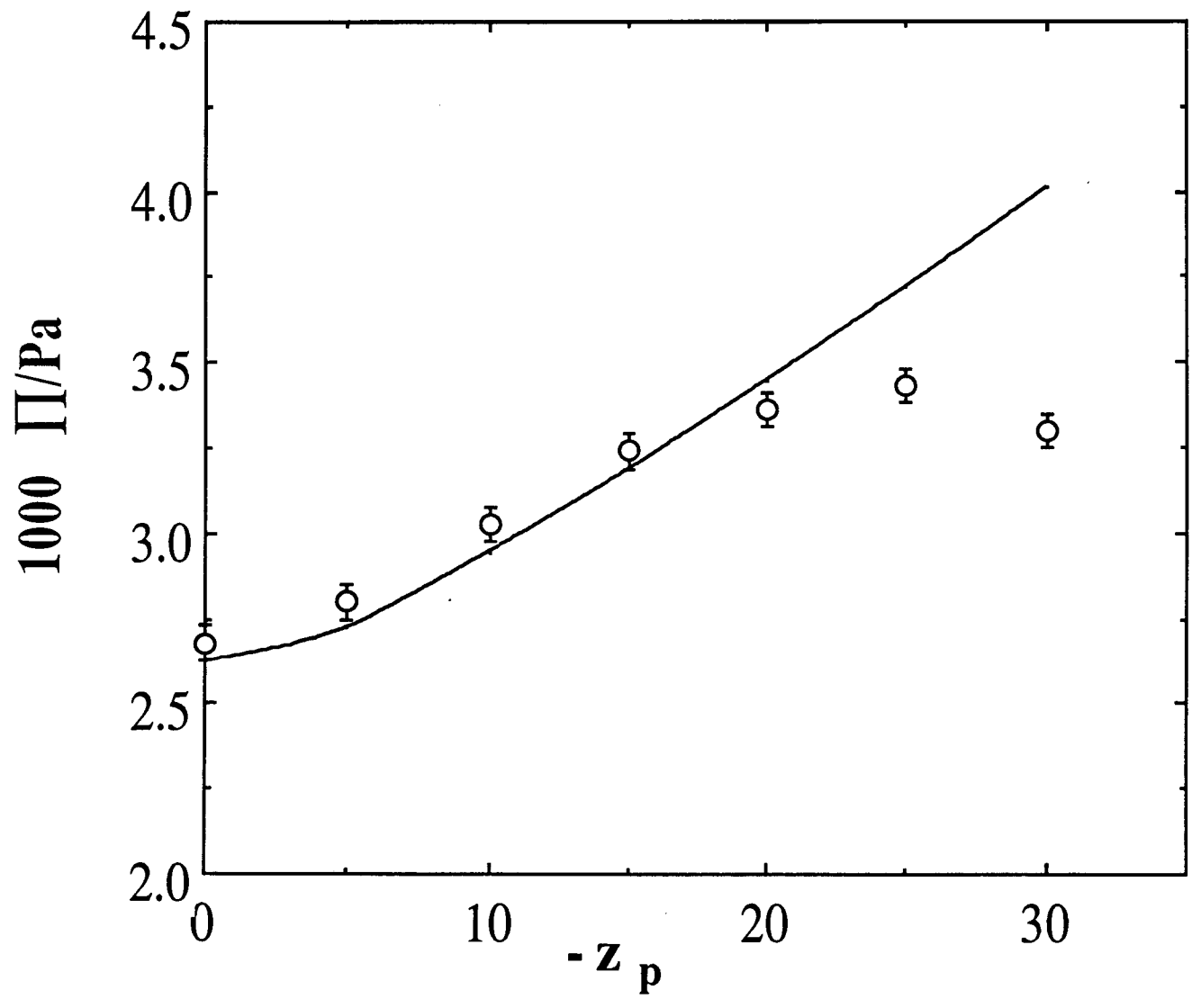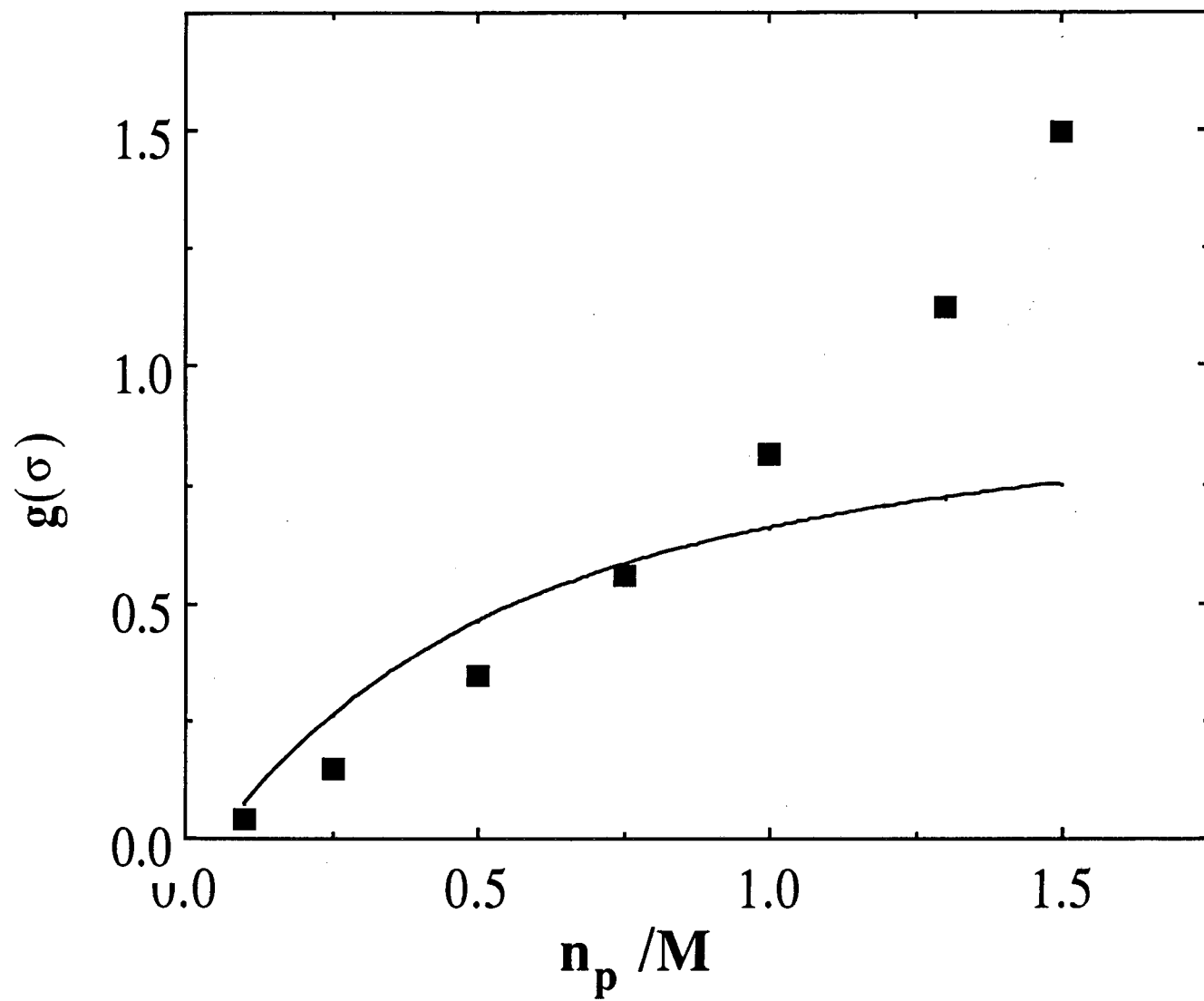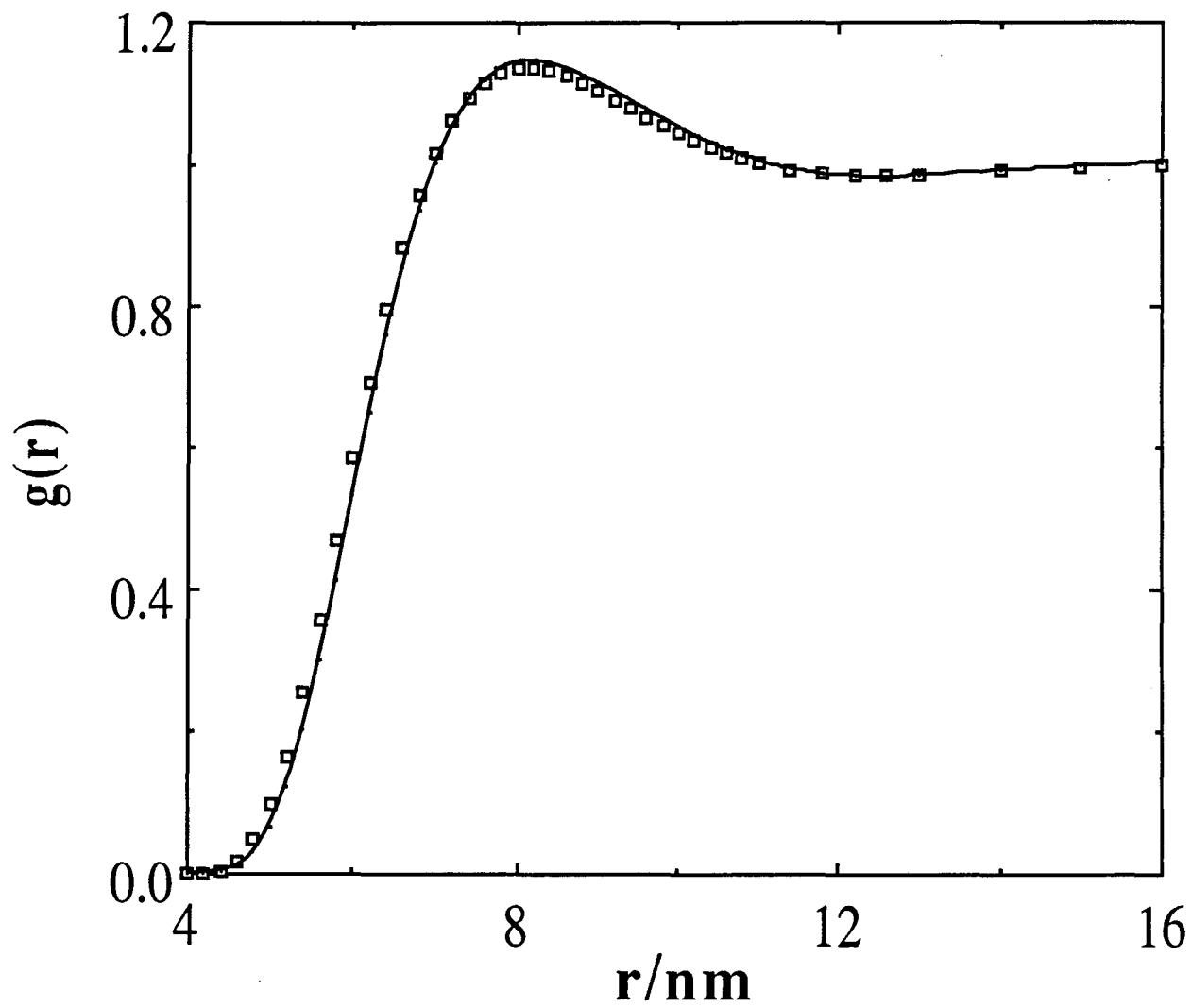
FIGURE 1

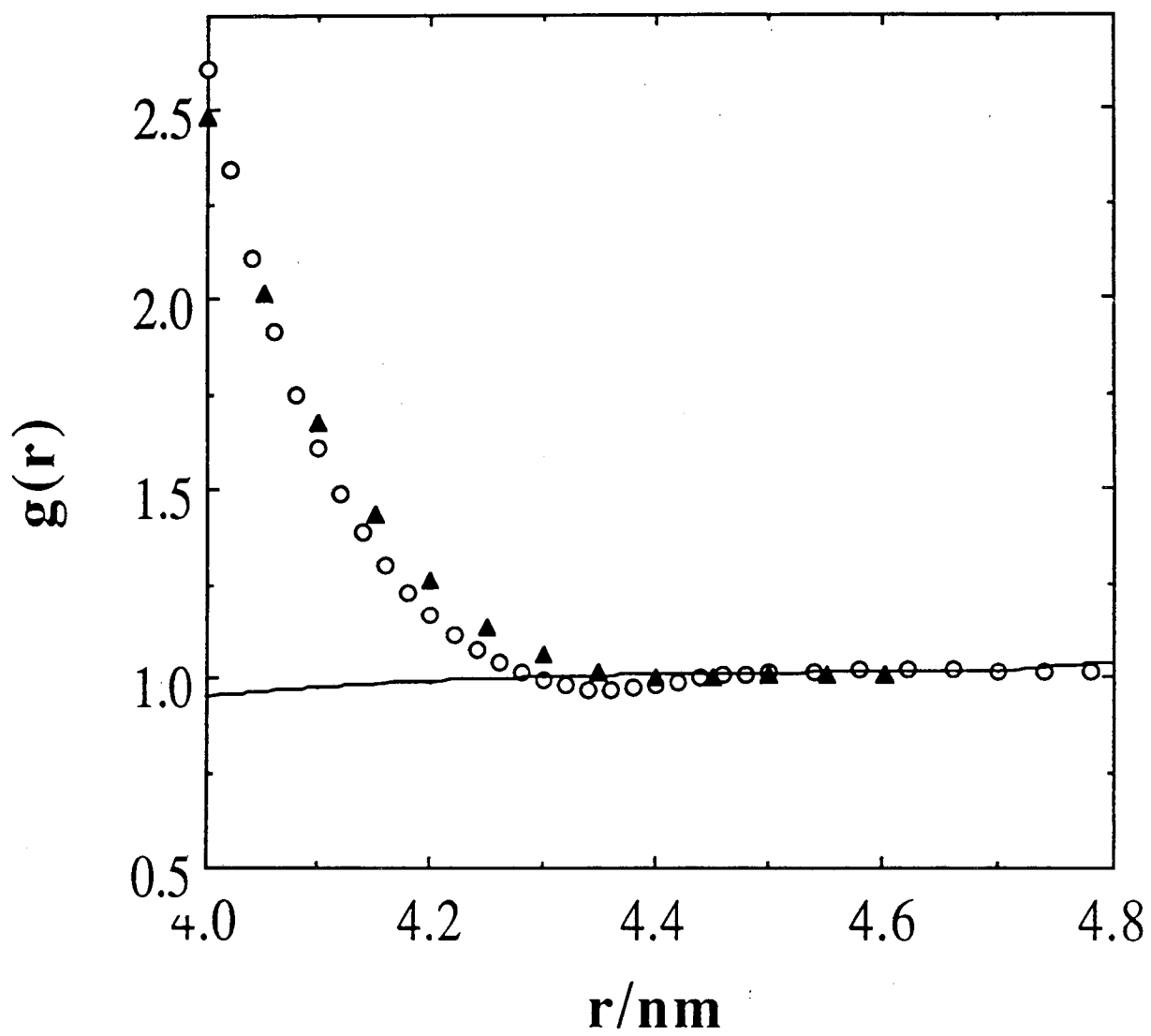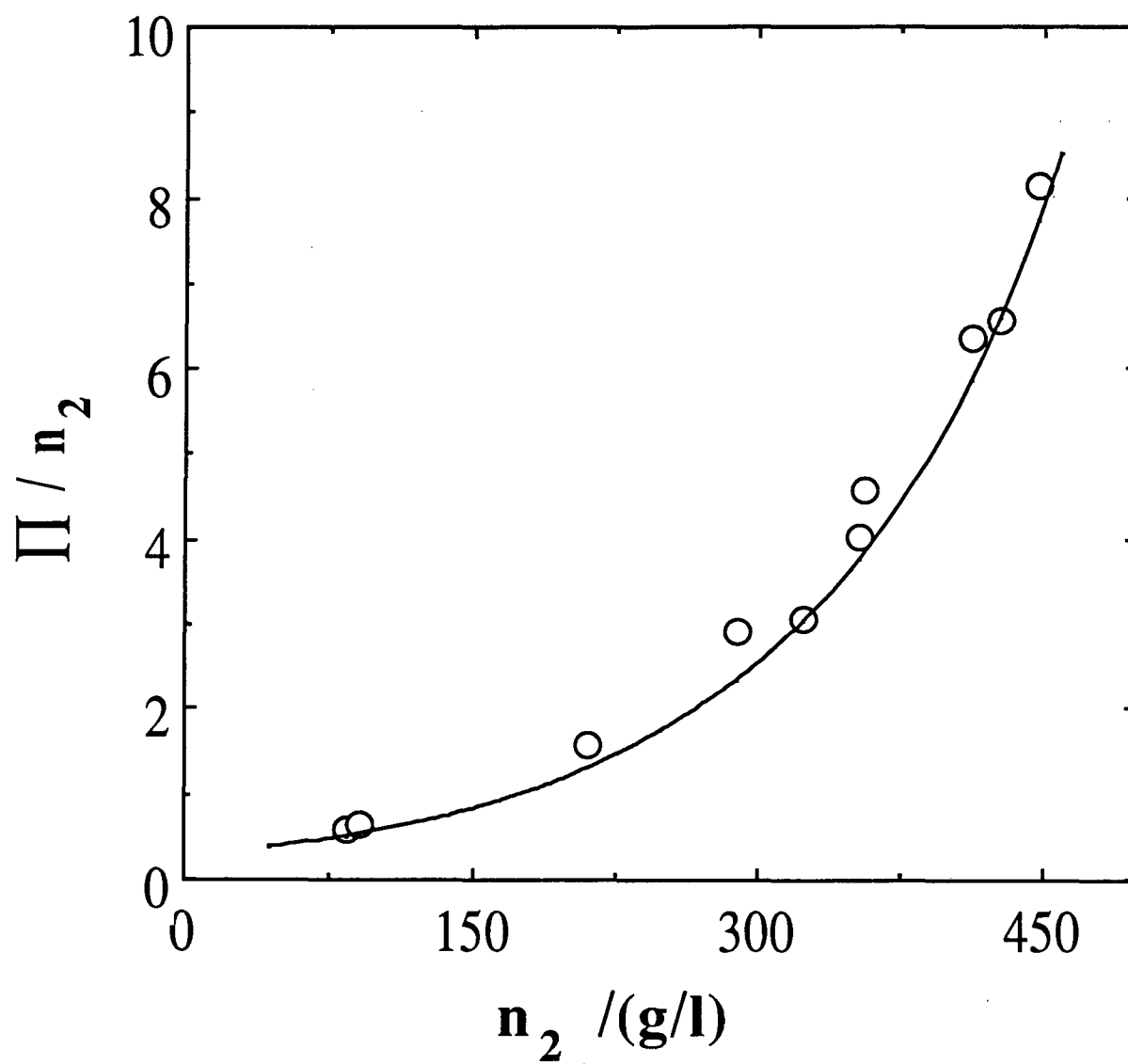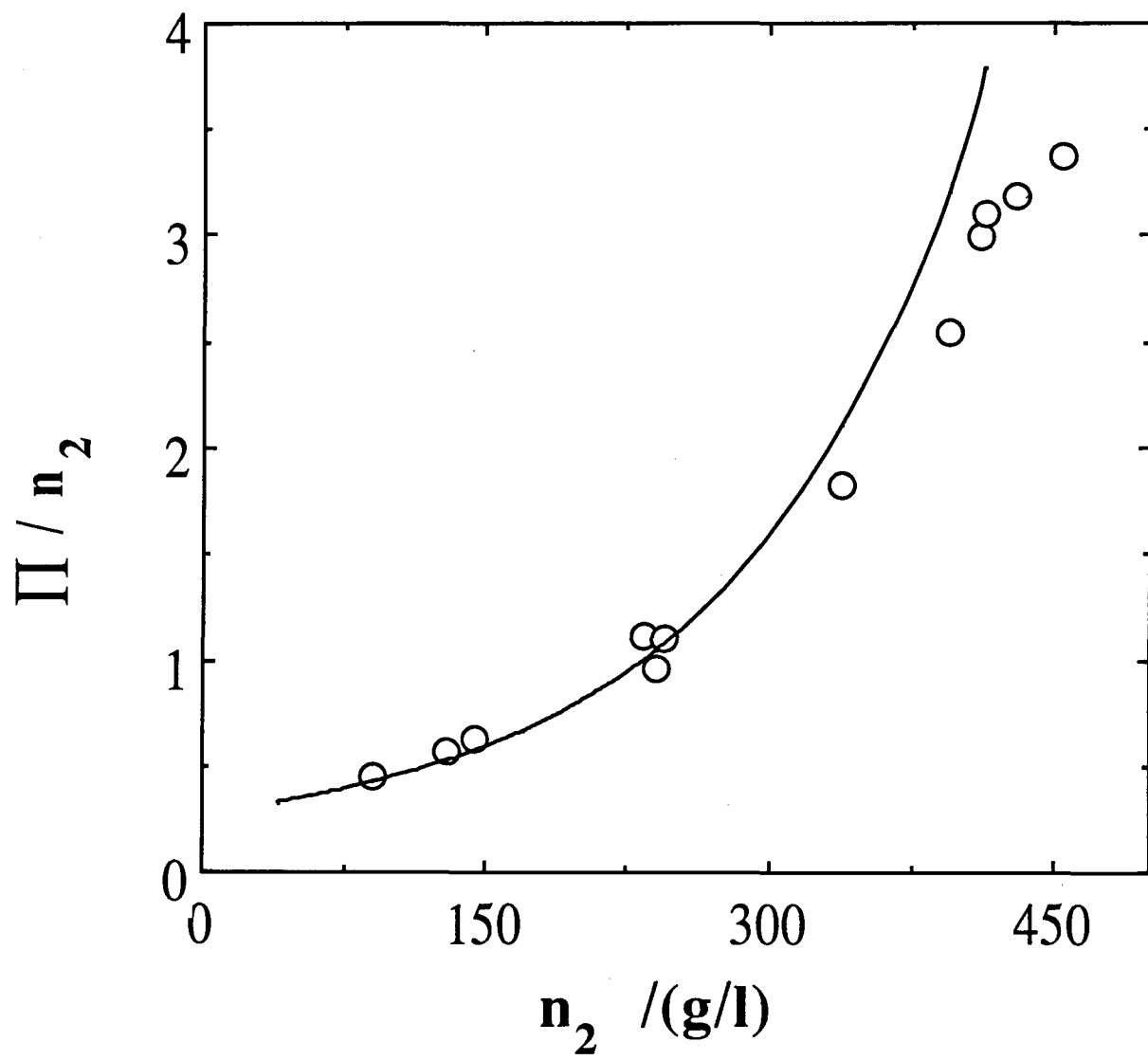FIGURE 2

FIGURE 3

FIGURE 4a

FIGURE 4b

FIGURE 5

FIGURE 6

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720