Donnan phenomena in membranes with charge due to ion adsorption. Effects of the interaction between adsorbed charged groups

Salvador Mafé,[a] José A. Manzanares,[a] and Howard Reiss
Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024

A physical model for the modified Donnan phenomenon associated with ion adsorption on localized membrane sites is presented. This model accounts for the dependence of the concentration of adsorbed ions on electrolyte concentration and pH as it is influenced by the electrostatic interaction between adsorbed ions. The equilibrium thermodynamic concepts employed are based on the Donnan formalism for the ion equilibria between membrane and solution, and the Bragg–Williams approximation for an adsorption isotherm that incorported interaction between adsorbed ions. Our results include the concentration of charged groups in the membrane, the pH of the membrane phase solution, and the Donnan potential as functions of the pH and the electrolyte concentration of the external solution for different degrees of the electrostatic interaction. These magnitudes are of considerable interest in biopolymers, membranes, and conducting polymers.

I. INTRODUCTION

The presence of charged groups attached to the membrane structure plays a central role in many observed equilibrium and transport phenomena in biological[1] and synthetic membranes.[2] Charges can be due to the ionization of functional groups present in the membrane matrix,[3] as well as to the adsorption[4] of ions of external origin when the membrane is immersed in an electrolyte solution.

Ion adsorption in biopolymers,[1,5] membranes,[4,6] and conducting polymers[7–9] constitutes a problem of considerable experimental interest. A number of theories describing the thermodynamics of such adsorption phenomena have been advanced.[1,4,8,10,11] Most of these make use of the classical theory of the electrical double layer at charged interfaces.[1,3,5,6,10] Others[4,8] invoke the Donnan equilibrium theory. However, it seems that no theoretical study accounting simultaneously for the electrolyte concentration and pH dependence of reversibly adsorbed charged species on the one hand, and the electrostatic interaction between these species on the other hand, has been presented previously. The present paper addresses this problem.

Our model is simple. It is based on the Donnan formalism[1,8] for the ion equilibria, and makes use of the Bragg–Williams approximation[12,13] to estimate how interaction between the adsorbed charges influences the adsorption isotherm. The theoretical results predict the concentration of charged groups in the membrane, the pH of the membrane phase solution, and the Donnan potential (the electrical potential difference established between the membrane and the bathing solution) as functions of the pH and electrolyte concentration of the bathing solution for different degrees of electrostatic interaction between adsorbed charges. We also discuss the conditions under which such interaction is important enough to be considered. Given

the multidisciplinary nature of the problem, it is expected that the simplified model presented here will be useful as a starting point for more elaborate treatments that account for the special features of each particular case.

II. FORMULATION OF THE PROBLEM

Figure 1 illustrates the system to be studied. The external solution is designated as phase 1 and the membrane solution as phase 2. Subscripts 1 and 2 will denote the phases, while subscript 3 is reserved for the charged species adsorbed to the membrane matrix. We consider a ternary electrolyte, say NaCl–HCl–H$_2$O, in order to be able to treat the effects of both pH and electrolyte (NaCl). For simplicity, thermodynamic activities are replaced by concentrations, and we ignore the structural changes that the membrane may undergo as it is charged. Concentrations n, p, and r refer to sodium, hydrogen, and chloride ions, respectively. Finally, N symbolizes the concentration of adsorption sites in the membrane. All concentrations are expressed in mol/L (M) unless otherwise indicated.

At equilibrium, the respective electrochemical potentials of the various ions in phases 1 and 2 must be equal,[1,8] i.e.,

$$\mu^0_{n,1}+kT \ln n_1+e\phi_1=\mu^0_{n,2}+kT \ln n_2+e\phi_2, \quad (1a)$$

$$\mu^0_{p,1}+kT \ln p_1+e\phi_1=\mu^0_{p,2}+kT \ln p_2+e\phi_2, \quad (1b)$$

$$\mu^0_{r,1}+kT \ln r_1-e\phi_1=\mu^0_{r,2}+kT \ln r_2-e\phi_2, \quad (1c)$$

which leads to the set of equations

$$\ln(K_n n_1)=\ln n_2+\varphi_D, \quad (2a)$$

$$\ln(K_p p_1)=\ln p_2+\varphi_D, \quad (2b)$$

$$\ln(K_r r_1)=\ln r_2-\varphi_D, \quad (2c)$$

where K_j's are partition coefficients defined by

$$K_n=\exp[-(\mu^0_{n,2}-\mu^0_{n,1})/kT], \quad (3a)$$

[a]Permanent address: Departamento de Termodinámica, Facultad de Física, Universidad de Valencia, 46100 Burjasot. Spain.
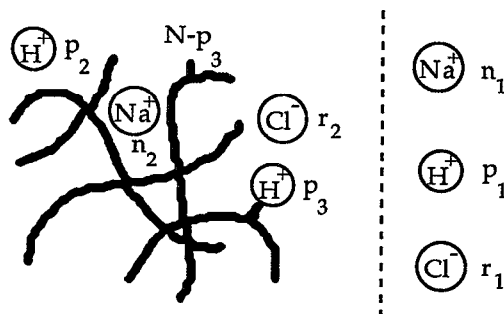
FIG. 1. Schematic view of the equilibrium problem dealt with.

$$K_p = \exp[-(\mu^0_{p,2} - \mu^0_{p,1})/kT], \qquad (3b)$$

$$K_r = \exp[-(\mu^0_{r,2} - \mu^0_{r,1})/kT]. \qquad (3c)$$

In Eqs. (2) and (3), the μ^0's refer to the standard-state chemical potentials while $\varphi_D \equiv e(\phi_2 - \phi_1)/kT$ is the Donnan potential in kT/e units established between the two phases, while k is the Boltzmann constant, T, the temperature, and e, the absolute value of the electronic charge. The NaCl and HCl concentrations can be varied arbitrarily, but the ion concentrations in Eqs. (2) are constrained by the respective bulk phase electroneutrality conditions,

$$n_1 + p_1 = r_1, \qquad (4)$$

$$n_2 + p_2 + p_3 = r_2. \qquad (5)$$

Now consider the interaction between adsorbed charges on neighboring sites. An exact treatment would require the computation of the configurational partition function, for the system of charges covering all possible arrangements on the available sites. This is a formidable problem, and so we elect to approximate this partition function using the Bragg–Williams model.[12,13] Thus we assume that the arrangement of particles is random (this would be the case in the absence of interaction). Proceeding in this way may not be quantitatively correct. In fact, there are approximations significantly better than the Bragg–Williams one, but it seems that this approximation is the simplest possible that retains the correct qualitative features.[13] For the adsorbed particles, the partition function in the canonical ensemble is derived as follows.[12] Let p_3/N be the fractional surface occupation. Suppose there are z sites surrounding any adsorbed particle. Then, an average number zp_3/N will be occupied by other particles, so that a total number of zp_3^2/N interacting pairs would result. However, we have counted each pair twice, and therefore the final number of interacting pairs is $zp_3^2/2N$, which gives an average total energy $wzp_3^2/2N$, w being the interaction energy assumed constant for one pair. Now, the partition function can be written as

$$Q = \frac{N!}{p_3!(N-p_3)!} \, q^{p_3} \exp\left(\frac{-wzp_3^2}{2NkT}\right), \qquad (6)$$

where q is the partition function for a single adsorbed particle and the preexponential factor is the number of arrangements of adsorbed particles on N sites. Equation (6) is the only equation throughout the present analysis where N and p_3 are expressed in particles per unit volume rather than in mol/L. Note that, in accordance with the Bragg–Williams method, the preexponential factor and the number of interacting pairs are evaluated as if the particles were randomly distributed among the sites. Once the partition function is available, calculation of the chemical potential of the adsorbed particles, and the derivation of the adsorption isotherm is immediate.[8,12] The result for the isotherm is, in our case,

$$\kappa p_2 = \frac{p_3}{N - p_3} \exp\left(\frac{u p_3}{N}\right), \quad u \equiv \frac{wz}{kT},$$

$$\kappa \equiv \exp[-(\mu^0_{p,3} - \mu^0_{p,2})/kT]/N, \qquad (7)$$

where $\mu^0_{p,3} = -kT \ln(qN)$ and the dimensionless energy is positive, since the interaction between the adsorbed charged species is repulsive. Note that $u = 0$ in absence of interaction, and Eq. (7) reduces to the well-known Langmuir adsorption isotherm[13,14] with adsorption constant κ. Adsorption isotherms having the dependence on the fractional surface occupation given by Eq. (7) are known as Frumkin isotherms in the electrical double layer literature.[15] More refined treatments for ion adsorption have been discussed,[1,10,16] though they apply mainly to "mobile" adsorption (e.g., ion adsorption at electrodes[16]) rather than to the localized adsorption involving membrane sites considered here.

Before proceeding to solve the system of equations, Eqs. (1)–(7), it is worthwhile to examine the conditions under which interaction between the adsorbed species should be considered. To this end, we estimate the electrostatic interaction energy between adsorbed charges for the case where u is a screened Coulomb potential,[7] and write

$$u = \frac{1}{kT} \frac{e^2 \exp(-r/L_{De})}{4\pi\epsilon r}, \quad L_{De} \equiv \left(\frac{\epsilon RT}{F^2 \sum_i z_i^2 c_i}\right)^{1/2}, \qquad (8)$$

where L_{De} is the Debye length[1] for the membrane solution phase, r is a typical distance between the adsorbed species, ϵ is the dielectric permittivity of the medium in which these groups are immersed, and the c_i are the ion concentrations in the membrane solution (F is the Faraday constant and R the gas constant; note that $kT/e = RT/F$). These inner concentrations can now be estimated from the Donnan equilibrium relationships.[1,2] For a uniunivalent electrolyte with charge numbers $z_1 = 1 = -z_2$, we have[1,2]

$$\sum_{i=1}^{2} z_i^2 c_i = 2\left[\left(\frac{X}{2}\right)^2 + c_0^2\right]^{1/2}, \qquad (9)$$

where X is the concentration of charged species in the membrane, and c_0, the concentration of ions in the bathing solution. Substitution of Eq. (9) into Eq. (8) yields

$$u = \frac{e^2}{4\pi\epsilon r kT} \exp\left\{-r\left(\frac{2F^2[(X/2)^2 + c_0^2]^{1/2}}{\epsilon RT}\right)^{1/2}\right\}. \qquad (10)$$

TABLE I. Electrolyte Debye length in the membrane phase solution, L_{De}, and the distance between adsorbed ions that makes $u = 1 (r_{max})$, as functions of the concentration of charged groups in the membrane, X, and the external electrolyte solution concentration, c_0.

| c_0 (M) | $X = 1$ M | | $X = 10^{-1}$ M | | $X = 10^{-3}$ M | |
	L_{De} (Å)	r_{max} (Å)	L_{De} (Å)	r_{max} (Å)	L_{De} (Å)	r_{max} (Å)
10^{-4}	1.55	4.04	4.90	8.91	48.5	29.8
10^{-3}	1.55	4.04	4.90	8.91	32.7	25.4
10^{-2}	1.53	4.01	4.85	8.86	10.9	14.6

Now, for electrostatic interaction to be important, u should be at least of order unity. This condition can only be met when the distance between the adsorbed particles is less than r_{max} obtained from Eq. (10) by solving for r after u has been set to unity. Table I gives the values of L_{De} and r_{max} derived from Eqs. (8)–(10) as functions of c_0 and X, using the values: $kT/e = 25.7$ mV, $F = 96500$ C/mol, and $\epsilon = 10\epsilon_0 = 8.85 \times 10^{-11}$ C/Vm for the various constants, where ϵ_0 is the vacuum dielectric permittivity. Note that the charged groups are attached to the polymer and, therefore, they "see" a dielectric constant smaller than that of bulk water.

Consider the results in Table I. If the average distance between adsorbed ions is $r > r_{max}$, then the interaction between them will be small, and the adsorption isotherm in Eq. (7) will tend to the Langmuir limit. According to Table I this will be the case for highly charged membranes ($X \approx 1$ M) immersed in concentrated electrolyte solutions. However, for weakly charged membranes ($X \approx 10^{-3}$ M) interaction effects can be important, especially when low electrolyte concentrations are used, since it is likely that $r \approx 10$ Å in many experimental situations (see, e.g., Ref. 7). Let us note finally that we have ignored the effects of conformational changes,[17] assuming that the adsorption of the ions on the sites produces no dramatic changes on the membrane structure. This assumption will be invalid when that structure is not rigid enough. Still, the above analysis presented may suggest the way to further refinements.

III. MATHEMATICAL SOLUTION

The equilibrium under consideration is characterized by five unknowns (n_2, p_2, r_2, p_3, and φ_D), whose values must be determined by the simultaneous solution of Eqs. (2), (5), and (7). Equation (4) simply establishes a relationship between the values of n_1, p_1, and r_1. The method of solution is as follows. First, substitute for n_2, p_2, and r_2 in Eq. (5) by using Eqs. (2) and obtain

$$K_n n_1 \exp(-\varphi_D) + K_p p_1 \exp(-\varphi_D) + p_3$$
$$= K_r r_1 \exp(\varphi_D). \tag{11}$$

This yields a quadratic equation in $\exp(\varphi_D)$, whose solution can be written in the form

$$\varphi_D = \ln \left\{ \frac{p_3 + [p_3^2 + 4K_r(n_1 + p_1)(K_n n_1 + K_p p_1)]^{1/2}}{2K_r(n_1 + p_1)} \right\}, \tag{12}$$

where we have substituted for r_1 from Eq. (4). Now, it is clear from Eqs. (2b) and (7) that

$$\kappa p_2 = \kappa K_p p_1 \exp(-\varphi_D) = \frac{p_3}{N - p_3} \exp\left(\frac{u p_3}{N}\right). \tag{13}$$

Elimination of φ_D between Eqs. (12) and (13) yields

$$\frac{2\kappa K_p K_r p_1(n_1 + p_1)}{p_3 + [p_3^2 + 4K_r(n_1 + p_1)(K_n n_1 + K_p p_1)]^{1/2}}$$
$$= \frac{p_3}{N - p_3} \exp\left(\frac{u p_3}{N}\right). \tag{14}$$

This is the desired result. Solving for p_3 will allow us to investigate the effects of the interaction parameter u between adsorbed ions as n_1, p_1, and κ are varied, while the parameters K_n, K_n, K_r, and N remain constant. Note that Eq. (14) has only one physical meaningful solution, and can be easily solved by standard numerical methods. Once the value of p_3 is known, Eqs. (12) and (2b) give the values of φ_D and p_2, respectively. Thus, the whole set of Eqs. (2), (5), and (7) can be solved without resorting to any additional simplifying assumption.

IV. RESULTS

We now present some of the results. We take $N = 10^{-2}$ M, since we expect the interaction effects to be most important for weakly charged membranes (see Table I). Also, we consider $K_n = K_p = K_r \approx 1$ for the simplicity of interpretation. It has been indicated previously[8] that when the K's are of this order of magnitude, their exact values exercise little influence on the Donnan phenomenon (Ref. 11 addresses the problem of partition coefficients having very different values). The adsorption constant κ is varied over a wide range of values, namely $\kappa = 10^2$, 10^4, and 10^6 M^{-1}, the two extreme values being the most interesting [$\kappa = 10^2$ M^{-1} when $\mu^0_{p,3} \approx \mu^0_{p,2}$, see Eq. (7)]. According to Eq. (7), they correspond to the limits $\kappa p_2 \lesssim 1$ and $\kappa p_2 \gg 1$ (saturation), respectively. Moreover, the HCl concentration is varied from $p_1 = 0$ to $p_1 = N = 10^{-2}$ M for the cases $n_1 = 0$, 10^{-3}, and 10^{-2} M. This permits the study of the influence of electrolyte concentration (NaCl) on adsorption. We present curves $p_3(p_1, n_1, u)$, $p_2(p_1, n_1, u)$, and $\varphi_D(p_1, n_1, u)$ for $u = 0$, 3, 6, and 9. In accordance with our above estimate, these levels of interaction correspond to $r_{max} = 9.11$, 5.85, and 4.37 Å when substituted into Eq. (10) with $X = 10^{-2}$ M and $c_0 = 5 \times 10^{-3}$ M. Therefore, $u = 9$ may be considered as unrealistically high, and it is
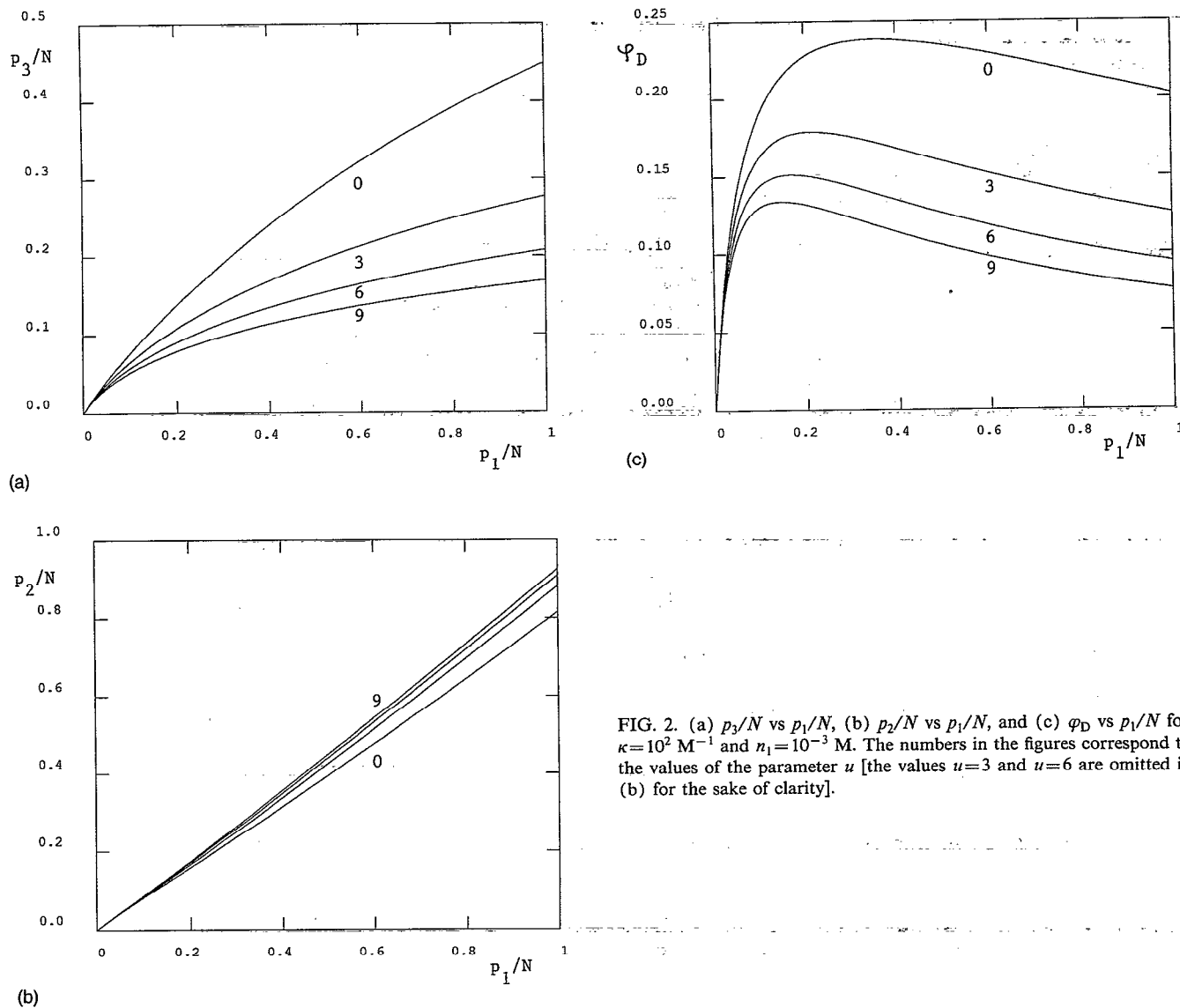
FIG. 2. (a) p_3/N vs p_1/N, (b) p_2/N vs p_1/N, and (c) φ_D vs p_1/N for $\kappa = 10^2$ M^{-1} and $n_1 = 10^{-3}$ M. The numbers in the figures correspond to the values of the parameter u [the values $u=3$ and $u=6$ are omitted in (b) for the sake of clarity].

presented only as a limiting case. Likewise, the opposite limiting case, $u=0$ (absence of interaction) is also presented for comparison.

Figures 2 ($\kappa = 10^2$ M^{-1}, $n_1 = 10^{-3}$ M), 3 ($\kappa = 10^4$ M^{-1}, $n_1 = 10^{-3}$ M), 4 ($\kappa = 10^6$ M^{-1}, $n_1 = 0$ M), and 5 ($\kappa = 10^6$ M^{-1}, $n_1 = 10^{-2}$ M) are a survey of our results. The numbers in the figures denote the associated values of u. The general trends may be summarized as follows.

A. p_3 and p_2 versus p_1 curves

The increase of p_3 with p_1 is clearly reduced as u is increased (see curves 2a–5a). As anticipated previously,[8] addition of NaCl ($n_1 \neq 0$) significantly increases hydrogen ion adsorption beyond that observed for the case $n_1 = 0$ for which $\kappa p_2 \gg 1$ (see curves 4a and 5a). On the other hand, the increase of p_2 with p_1 does not seem to be affected dramatically by interaction between adsorbed ions, although the effect, an increase, is slightly faster as u becomes larger (see curves 2b–5b). As expected, the pH is greater within the membrane than in the external solution.

Note, finally, that the interaction between the adsorbed ions significantly modifies the adsorption isotherms, the interaction effect being quantitatively more important in the limit of low adsorption constant (see curves 2a–3a).

B. φ_D versus p_1 curves

Again, we see that electrostatic interaction significantly changes the values of the Donnan potential, especially in the limit of low adsorption constant (see curves 2c–3c). The shape of the φ_D vs p_1 curves can easily be explained if we consider the following limiting cases of Eq. (12),

$$\varphi_D \approx \begin{cases} \ln\left[\dfrac{p_3}{2p_1} + \left[\left(\dfrac{p_3}{2p_1}\right)^2 + 1\right]^{1/2}\right], & p_1 \gg n_1, \quad (15a) \\ \\ \ln\left[1 + \dfrac{p_3}{2n_1}\right], & p_1 \ll n_1 \quad (15b) \end{cases}$$

Equation (15a) predicts that φ_D decreases with p_1 for large enough p_1, since p_3/p_1 decreases with p_1 in this limit (see curves 2a–5a). This is the general rule observed in φ_D for high p_1 values (see curves 2c–5c). Equation (15a) also
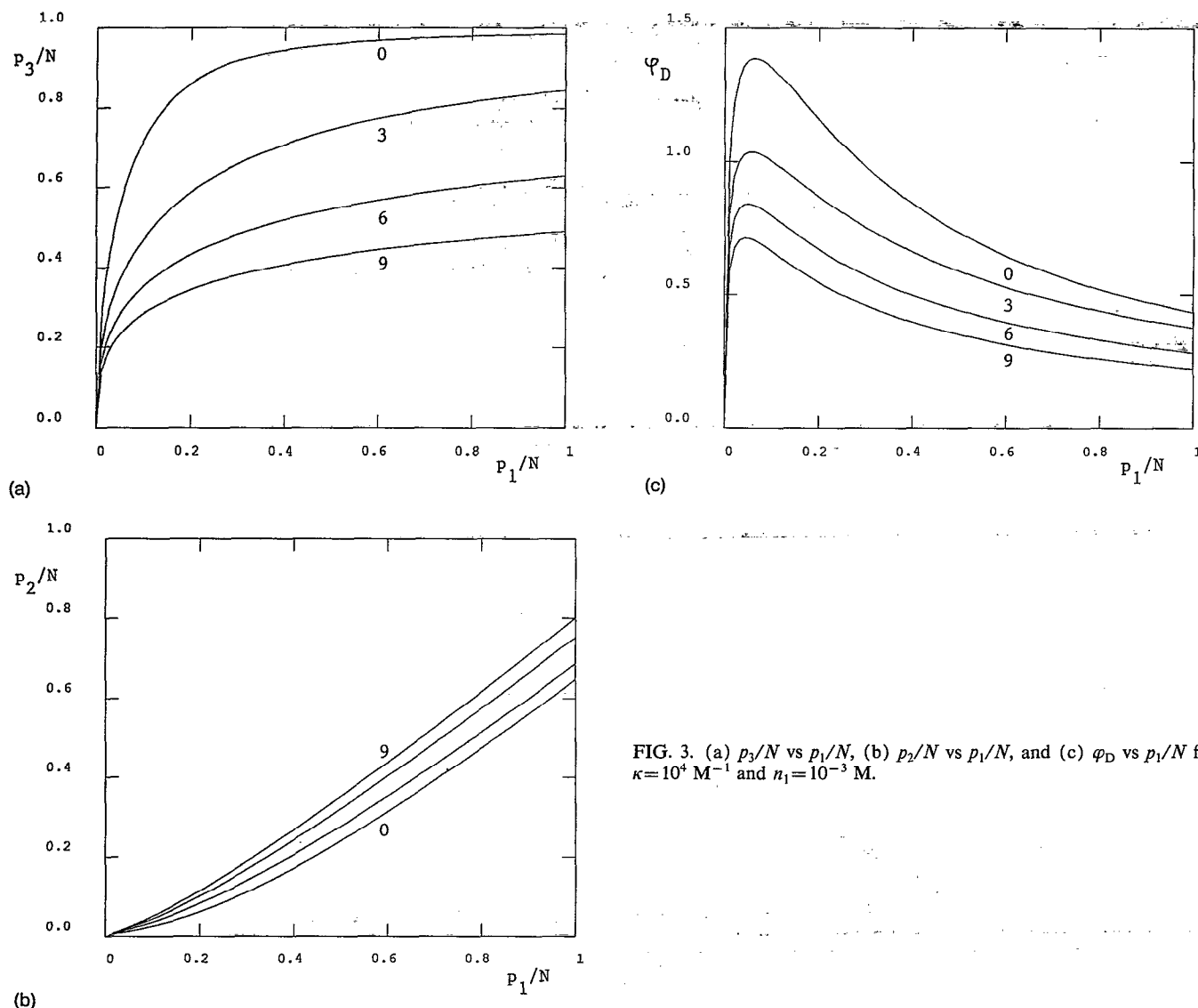
(a)

(c)

(b)

FIG. 3. (a) p_3/N vs p_1/N, (b) p_2/N vs p_1/N, and (c) φ_D vs p_1/N for $\kappa = 10^4$ M^{-1} and $n_1 = 10^{-3}$ M.

applies for small values of p_1 when $n_1 = 0$. Note that when $p_1 \to 0$, p_3/p_1 assumes a constant value (see curves 2a–5a). Thus, we see from Eq. (15a) that in the case $n_1 = 0$, the limiting value of φ_D when $p_1 \to 0$ is different from zero (see curve 4c). On the other hand, Eq. (15b) gives the limit $\varphi_D \to 0$ as $p_1 \to 0$ (and then $p_3 \to 0$), provided that n_1 is constant. According to Eq. (15b), φ_D will increase with p_1 when $p_1 \ll n_1$. These are indeed the cases, as shown in curves 2c, 3c, and 5c.

The experimental fact[8,9] that the addition of electrolyte (NaCl here) causes greater hydrogen adsorption (see curves 4a and 5a) can now be rationalized on the basis of curves 4c and 5c. Indeed, the minimum value of the Donnan potential in the absence of NaCl (curve 4c) is very similar to the maximum value of this potential in the presence of NaCl (curve 5c). Since the sign of φ_D is such that it favors hydrogen desorption, a higher adsorption should be expected for the smaller φ_D values, as is the case. Note that for $p_1 \approx N$, the φ_D values in curves 4c and 5c are of the same order of magnitude, and then the effect of the NaCl addition on adsorption is much smaller.

V. DISCUSSION

We have derived an equilibrium theory for the ion adsorption on localized membrane sites, which accounts for interaction between the adsorbed ions. The theory uses the Bragg–Williams approximation for the adsorption isotherm. The question arises if the charged synthetic membrane considered here behaves qualitatively differently from a polyion chain. If the polymer network constituting the membrane were lightly cross-linked, no such difference would be observed and spatial correlations among adsorbed ions would be described as linear along the contour of a single polymer chain. However, most charged synthetic membranes and conducting polymers are not "lightly cross-linked" and the three-dimensional Bragg–Williams approach could retain the correct quantitative features.

Despite its simplicity, the theory may find an application in a number of problems, where the concept of "charged membrane" is invoked.[1-9] However, we find it difficult to make a *quantitative* comparison of our theory
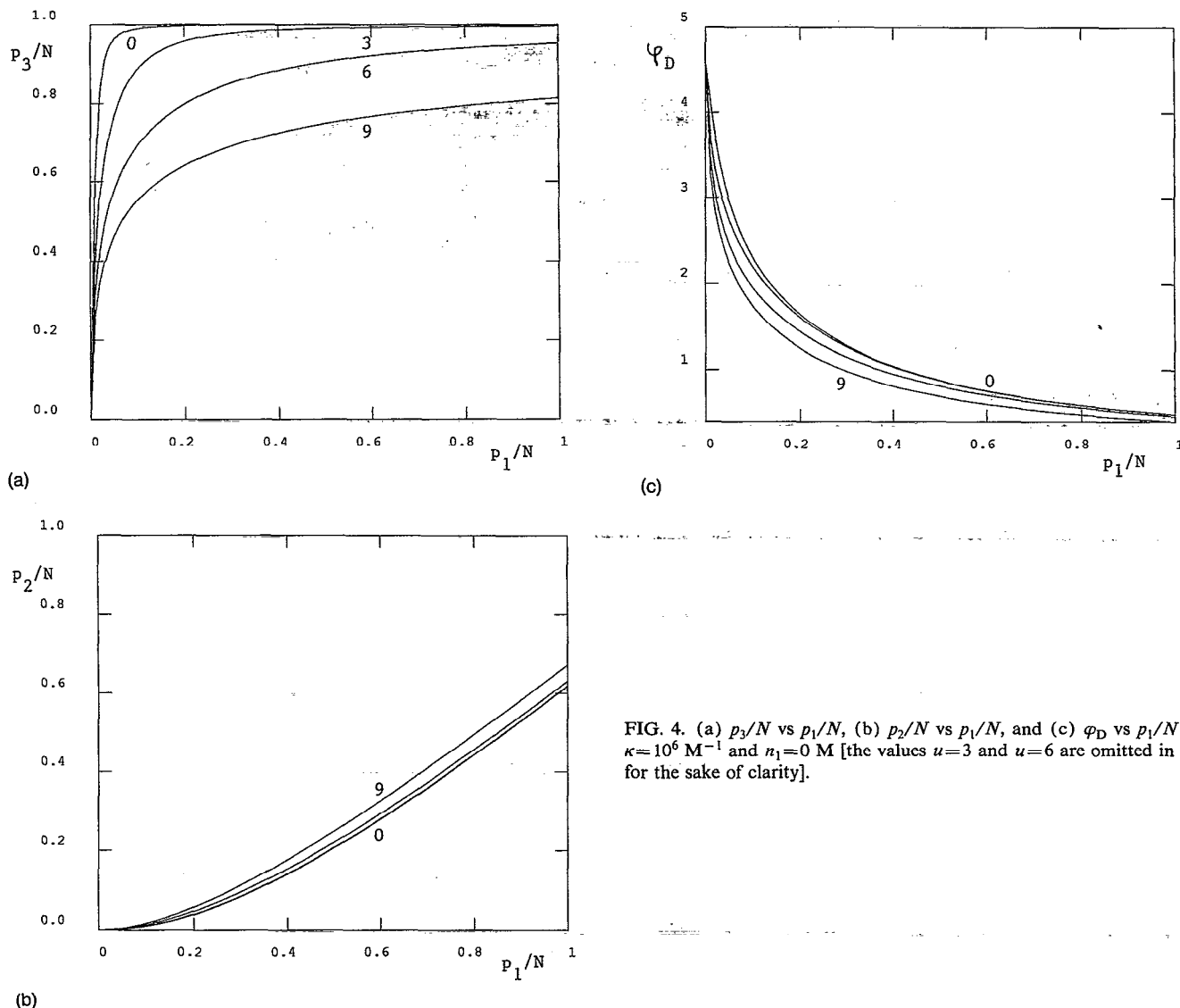
(a)

(b)

(c)

FIG. 4. (a) p_3/N vs p_1/N, (b) p_2/N vs p_1/N, and (c) φ_D vs p_1/N for $\kappa = 10^6$ M^{-1} and $n_1 = 0$ M [the values $u = 3$ and $u = 6$ are omitted in (c) for the sake of clarity].

with other theoretical or experimental approaches. Verbrugge and Pintauro[18] introduced an adsorption isotherm accounting for the interaction between ions in adjacent sites in their study of the electric potential profile in the pores of an ion-exchange membrane. However, these authors ignored this interaction in their analysis of the effect of ion adsorption on the profile of the electric potential within a pore, possibly because they were mainly interested in other effects related to changes in the dielectric constant.[18] On the other hand, although the adsorption isotherm derived here deviates significantly from the Langmuir isotherm for large enough values of the interaction, the fact remains that both isotherms behave similarly in the limit of low external HCl concentration, especially if the level of interaction is small.

There are, however, some qualitative features that deserve comment. The first refers to the role of the dielectric constant. In their study of nonaqueous electrokinetic transport in charged porous media, Westermann-Clark and Christoforou[6] found experimentally that the absolute value of the adsorbed pore charge (due to chloride ions in their case) decreased when the solvent dielectric constant was decreased. Indeed, chloride ion adsorption was clearly inhibited in pure methanol. No conclusive explanation for this behavior was offered. It is risky to attempt a comparison between their results and our model, since the pore charge was due to both adsorption of chloride ions and dissociation of the functional groups present in the membrane matrix.[6] All we can say is that according to our model, small values of the dielectric constant can lead to high values of the interaction parameter u. Therefore, it seems plausible that the ion adsorption would be smaller for the solvents employed in Ref. 6 than for solvents with high dielectric constant (e.g., water). These effects should be even more important for adsorbed ions of higher charge. Note finally that there seems to be an increased interest in the Donnan phenomena (particularly for the Donnan potential) in the field of conducting polymers.[7-9] In fact, the question of the interaction between the adsorbed ions in the polymer has already been mentioned in this context.[7,19] It is worthwhile to indicate that our model predicts a Donnan potential very sensitive to this interaction when $n_1 \neq 0$.
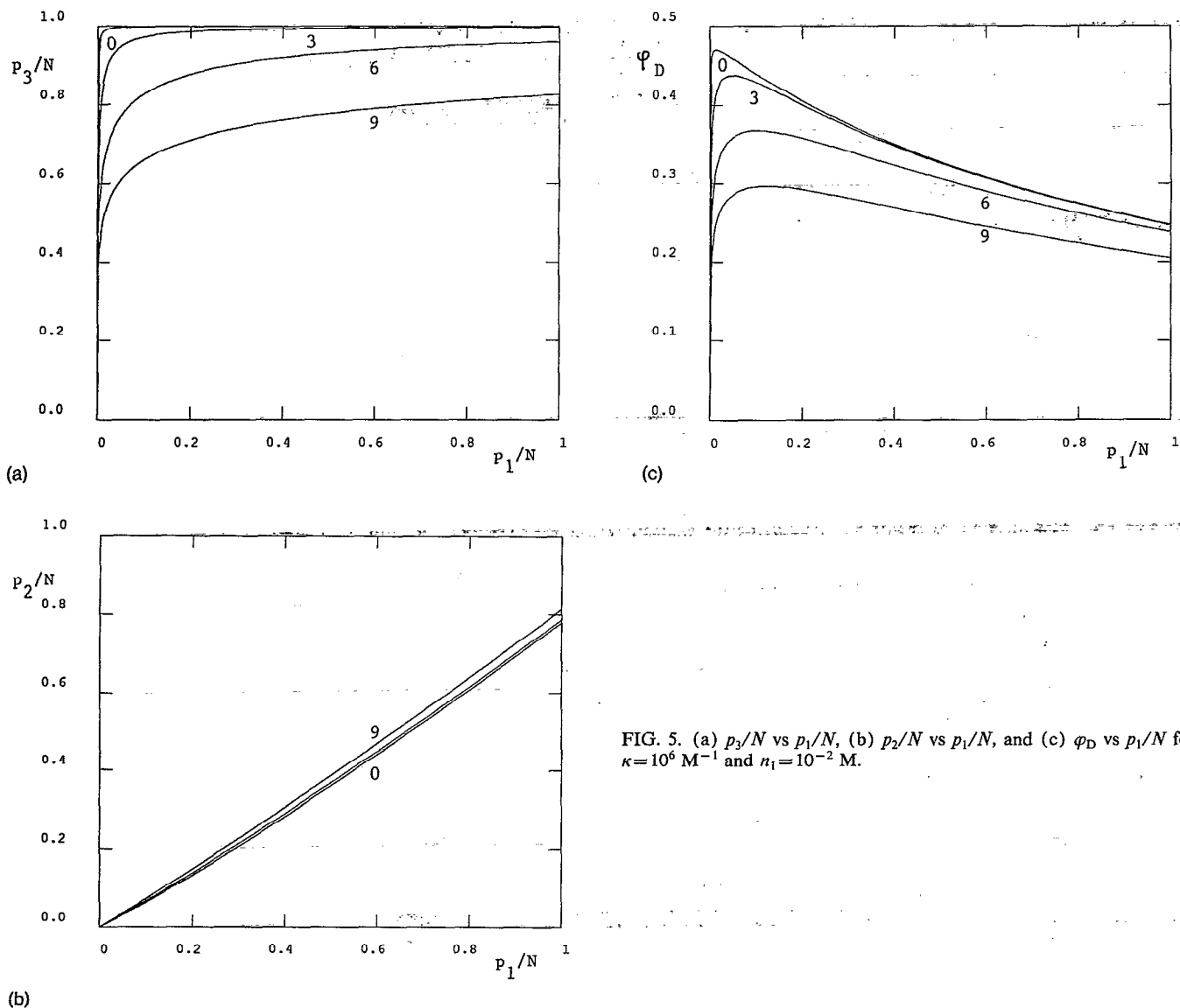
FIG. 5. (a) p_3/N vs p_1/N, (b) p_2/N vs p_1/N, and (c) φ_D vs p_1/N for $\kappa = 10^6$ M^{-1} and $n_1 = 10^{-2}$ M.

The present study constitutes a further step in the formulation of "modified Donnan phenomena" theories[8] relevant to the field of conducting polymers.

ACKNOWLEDGMENTS

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