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Review

COMPARISON AND DISCUSSION OF SOME THEORIES OF THE EQUILIBRIUM ELECTRICAL DOUBLE LAYER IN LIQUID ELECTROLYTES *

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ABSTRACT

Much past work on equilibrium properties of the electrical double layer is discussed. Particular attention is given to attempts to explain the differential capacitance of the double layer, with and without specific adsorption. Many theories of the inner and outer parts of the double layer are discussed, including continuum, discrete, and lattice gas models. It is concluded that although adequate theories of the diffuse part of the double layer exist, none available so far is entirely adequate for the inner layer because of the strong lateral interactions present in it.

(I) INTRODUCTION

This paper deals with the electrical double layer (EDL — see list of acronyms at end of the paper) in thermal equilibrium. It is thus primarily concerned with the structure of the double layer, interactions between its discrete ionic and molecular components, and with its quasi-static, measurable differential capacitance. By contrast, the succeeding paper involves the steady-state, small-signal ac response (without or with dc bias) of systems involving double layers near electrodes. Such response, and its analysis, has been termed Impedance Spectroscopy [1,2]. When measurements are not limited to equilibrium conditions, important kinetic effects may occur. Long ago, Frumkin [3] first pointed out the importance of the EDL in affecting heterogeneous electron transfer reactions. The presence of an EDL affects the reaction because the electric field conditions in the reaction region near the electrode are different from those in the bulk of the material.

The present paper is concerned primarily with nearly zero frequency response, and the second one with response covering a frequency range from low, and

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possibly very low, frequencies up to a MHz or so. The two papers are thus somewhat complementary as well as loosely coupled.

The electrical double layer present in nearly all solid and liquid materials, in which charge motion and translation are possible, is a complicated beast and its behavior is by no means fully understood theoretically. In its simplest form it involves a space charge region (the diffuse part of the double layer) beginning at the boundary of a conducting material and decreasing away from the boundary into the material. The charge involved may be electronic, ionic, or mixed and the resulting polarization may involve mobile charges of a single sign or of both signs. The distributed charge in the material is balanced by an equal and opposite charge on the surface or on an electrode if one is present. One general definition of the EDL is [4] "An electrical double layer is a non-homogeneous region of finite thickness containing significant variation in charge density across its thickness which consequently produces a potential drop across this dimension; the non-homogeneity invariably arises as a consequence of the competition between entropy and energy effects in the system's attempt to minimize its free energy".

The EDL plays an important role in the electrical behavior of semiconductor and electrochemical systems. The latter can include single crystals with intrinsic disorder and/or aliovalent doping, polycrystalline or composite solid electrolytes, fused salts, aqueous solutions, colloids, membranes, and even living cells. The interface at which an EDL appears may be that between the conducting material and air or vacuum (the resulting EDL is known as a Frenkel layer in solid materials); it may be an internal interface in the material; or it may appear between the material of interest and an electrode. In this work, the main emphasis will be on ionic EDLs in liquid or solid electrochemical systems with metallic electrodes, and more attention will be paid to unsupported than to supported systems.

The EDL is often studied under essentially equilibrium conditions, achieved by the use of a completely blocking (ideally polarizable) electrode. Because there have been many reviews dealing with the EDL [e.g., refs. 4, 5 (and references therein), 6 (contains a listing, often with some evaluation, of all major reviews to the date of writing), 7 and 8], the present discussion is selective rather than exhaustive, dealing with a bird's-eye view of a few specific areas and emphasizing still unsolved problems.

(II) THE EQUILIBRIUM DOUBLE LAYER

To begin with it is worthwhile to make some distinctions between various types of equilibrium EDL models (m): continuum (c) or discrete (d) models and primitive (p) or non-primitive (n) (civilized?) models. In recent years a primitive model has come to mean one in which the solvent molecules are replaced by a dielectric continuum with dielectric constant ϵ_s . The ions may be treated in the continuum approximation (a continuum primitive model: cpm) or discretely (dpm). Thus the cpm is a full cm. In contra-distinction, the nm is a full dm since both solute ions and solvent molecules are treated discretely, with the molecules usually taken as

having permanent dipole moments (usually of infinitesimal length: i.e. ideal point dipoles). If more than one conceptually different part of the EDL is defined, these characterizations may need to be applied separately to the individual parts, adding further complexity.

(II.a) Continuum models

The earliest models of the electrochemical EDL involve several simplifying assumptions. First, a continuum approximation is made: mobile ions are taken to be of infinitesimal size and their charge is smeared out, eliminating all ionic discreteness effects. Only quantities averaged over planes parallel to the electrode thus appear. Second, the solvent is represented by a uniform dielectric constant ϵ_s , often taken as the bulk value of the solvent material, ϵ_B . Thus one is dealing with a cpm. Finally, the charge on the (metal) electrode, taken flat and smooth, is assumed to be confined to the electrode surface plane (ESP), a region of zero thickness. Thus the character of the electrode, assumed to be a perfect conductor, plays no role in the response. Progress in double layer theory has involved the gradual transcendence and elimination of these idealizations as more and more interactions are included in the analysis.

The prototype theory embodying the above assumptions is that of Gouy [9] and Chapman [10]. A very important quantity which is often used to characterize the equilibrium EDL is the total differential capacitance of the system, C_T , usually expressed as capacitance per unit area of electrode, a practice we shall follow here by generally suppressing the distinction between total capacitance (or charge) and capacitance (or charge) per unit area, the more significant theoretical quantity. For a diffuse layer with total net charge Q_d and a total potential difference across it of ψ_d , the corresponding differential capacitance, C_{dl} , is just $-dQ_d/d\psi_d$. This quantity may often be determined from measurements and is easy to calculate from the Gouy–Chapman (GC) theory. Unfortunately, theory and experiment only approach good agreement in the limit of small ionic concentration.

The next major advance in the area was made by Stern [11] who took some account of finite ion size by introducing the assumption that the distance of closest approach to the electrode of the diffuse layer ions (taken of equal size, diameter $2r_i$) is r_i , the distance between the centroid of ionic charge of ions nearest the electrode and the ESP. Finite ion size was, however, neglected in the rest of the diffuse layer. This model, the GCS, is perhaps most appropriate for solid electrolytes at relatively low ionic concentration. For liquid electrolytes, however, diffuse layer ions nearest the electrode are solvated (in the absence of specific adsorption), and it is thus usually assumed that there is a single layer of solvent molecules between the nearest ions and the ESP [12,13]. In later work [14], it was assumed that the ESP lies somewhat inside the physical surface of the metal to account for field penetration into the electrode, adding a small additional increment (d_p) to the effective electrical thickness of the charge-free inner layer next to the electrode. The outer Helmholtz plane (OHP) marks the boundary between this layer and the diffuse space charge region.

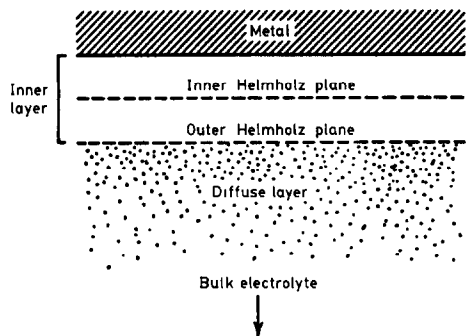


Fig. 1. Schematic representation of the EDL (reprinted by permission of John Wiley and Sons, Inc., copyright © 1967 [6,15]).

In the presence of specific adsorption (defined in crude terms as the existence of partly chemically bound solute ions located as close to the ESP as allowed by steric constraints), even the completely blocking situation is more complicated. Specifically adsorbed ions have lost their solvation shells in the direction of the electrode so that the effective distance between the ESP and the charge centroids of such ions, located at the inner Helmholtz plane (IHP), is $d_p + r_i$. The situation is shown diagrammatically in Fig. 1 and with pertinent quantities defined in Fig. 2 (see refs. 5 and 16 for justification and more detailed discussion of the EDL model implied by this figure). In Fig. 2 the ϵ s are local dielectric constants (generally much smaller than ϵ_B because interactions in these planar regions are quite different from ordinary bulk-material interactions); the σ s are charges per unit area; and the ψ s are local potentials. It is quite clear from Figs. 1 and 2 that the EDL in liquid electrolytes is far from being just a simple two-component layer made up of the diffuse region and compensating charge on the electrode. When specifically adsorbed ions are of appreciably different sizes than solvent molecules, the model must be made even more complex [5].

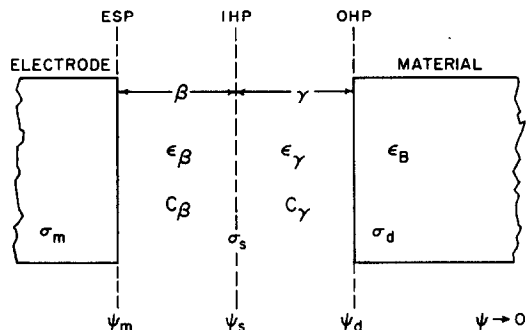


Fig. 2. Definitions of various quantities in electrode-interphase region of the EDL [5,16].

(II.a.1) No specific adsorption

(a) *Early work.* In the absence of adsorption the GCS model predicts that the total differential capacitance, C_T , is related to the inner layer capacitance, C_H , and the diffuse layer differential capacitance, C_{dl} , through the equation

$$C_T^{-1} = C_H^{-1} + C_{dl}^{-1} \quad (1)$$

where γ may be taken zero and $C_H = C_\beta$ in Fig. 2 for this situation. Thus if C_T is derived from quasi-equilibrium measurements and C_{dl} is calculated from an appropriate theory, C_H may be obtained. Note that in the present situation C_H should be concentration independent. No geometric capacitance, C_g , need appear in eqn. (1) because we are concerned only with single-electrode effects here. Now modern analysis of the electrochemical EDL may be said to have its inception and underpinning with the work of Grahame, especially his careful and accurate measurements on NaF in an aqueous solvent for a range of temperatures, applied potentials, and electrode charge [17,18]. NaF is particularly appropriate because it shows less specific adsorption on anodic polarization than most other solutes. Grahame used ordinary GC diffuse layer theory and eqn. (1) to derive C_H as a function of the above variables; some of his results are presented in Fig. 3. It is particularly noteworthy that C_H is very far from being independent of electrode charge, $\sigma_m (= -\sigma_d)$, and temperature. It is the detailed structure of C_H which leads to much of the interest and challenge in understanding the equilibrium EDL.

Some of Grahame's NaF C_T data are presented in Fig. 4. The dashed line shows a fit using GC diffuse layer theory alone. It is clear that it is inadequate and thus the effects of an inner (or compact) charge-free region must not be neglected. The first

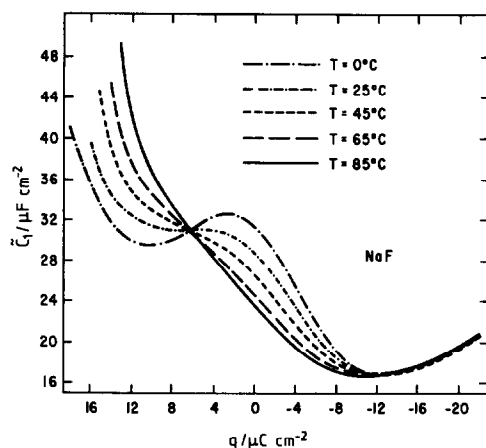


Fig. 3. Differential capacitance of the inner layer, $\tilde{C}_1 \equiv C_H$, vs. electrode charge ($q = \sigma_m$) (reprinted with permission [5,14]). Data calculated by Grahame [17,18] from his experimental results using a dropping mercury electrode and assuming no specific adsorption.

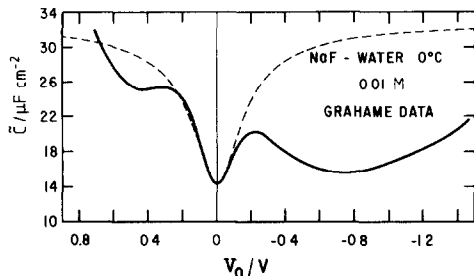


Fig. 4. Total differential capacitance of the EDL, $\tilde{C} \equiv C_T$, vs. applied p.d., $V_0 \equiv \psi_m$, based on data of Grahame [18] and showing diffuse layer fit (---).

full analysis of the Grahame C_T data was produced by the present author [13] and was later improved and extended [14]. The first treatment was carried out completely in the spirit of the continuum approximation and involved the assumption of dielectric saturation in both the diffuse layer and the inner monolayer of water molecules next to the electrode. In addition, compression of this monolayer under the high electric field in the inner region was included as well. Such electrostriction leads to a dependence of inner layer solvent number density on σ_m . A defect of this kind of approach, however, beyond its neglect of discreteness effects, is the presence of several semi-macroscopic parameters, applied to a microscopic situation, along with the necessity of determining some parameter values from the data themselves rather than from other independent measurements. Nevertheless, good fitting results were obtained using physically reasonable parameter values, shedding some light on inner layer behavior. The separate effects of dielectric saturation and layer compression are illustrated in Fig. 5, as well as the overall fit obtained for cathodic polarization when both effects are present.

The approach of ref. 13 was improved in various ways in ref. 14 and fitting carried out for a variety of temperatures. An important improvement over the earlier phenomenological calculations of inner-layer dielectric saturation was the treatment of the dielectric behavior of the inner layer in a somewhat more discrete fashion by approximating the water molecules as point dipoles able to rotate continuously under the influence of the effective electric field. But only average dipole behavior was treated, still a *cm*. In addition, imaging of dipoles in the electrode (single imaging) or in the electrode and the diffuse layer (infinite imaging, also called conductive-conductive imaging) was considered, as well as the presence of a "natural" field causing the dipoles to line up more in one direction than others even in the absence of applied fields (i.e. at the ECM potential, $\psi_m = V_0 = 0$, the point of zero electrode charge, pzc). Some possible sources of this field have been discussed in refs. 6 and 14, and the presence of such a natural field or potential has often been independently suggested since the earlier work (e.g., refs. 19, 20).

A weakness in the ref. 14 inner layer model is its neglect of dipole-dipole interactions; in addition, the assumption of arbitrary dipole orientations may be less

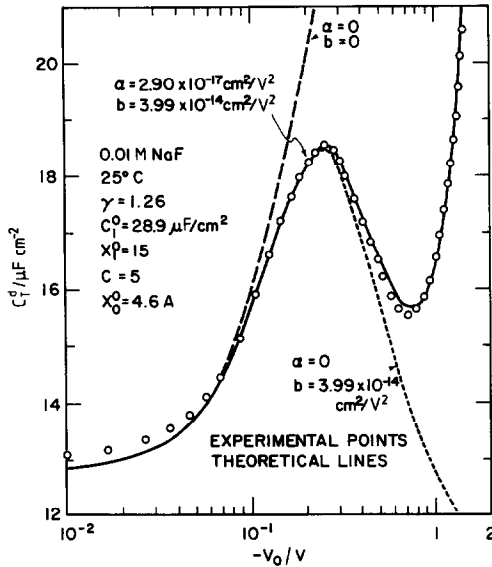


Fig. 5. Comparison of Grahame 25° C NaF $C_d^T = C_T$ results with continuum theory, showing effect of no compression and no dielectric saturation ($\alpha = b = 0$), no compression ($\alpha = 0$), and saturation and compression both present [13].

realistic in some real situations than the assumption that only a few orientations are possible. These matters will be discussed further below. In spite of the model's apparent weaknesses, it yielded excellent agreement with Grahame's data, better overall than that of any later treatments. Results are presented in Figs. 6 and 7; here curves for different concentrations have been successively displaced for clarity of presentation. The effects of some of the main physical processes included in the model are summarized in Fig. 8. The discrepancies apparent at appreciable positive potential differences (p.d.s) may arise from the presence of specific adsorption of F ions, behavior not included in the theory.

(b) *Dipoles in the inner layer and the Cooper-Harrison "catastrophe"*. There have been many treatments of the inner region of the EDL which approximate it as a single layer of solvent molecules whose electrical effects are modelled by point dipoles with n orientational states allowed. We have already discussed the early $n = \infty$ case [14], one which led to very good agreement with experiment over wide ranges of concentrations, temperatures, and applied potentials. At about the same time, Watts-Tobin [21] independently treated the $n = 2$ situation, although his comparisons with experiment were far less extensive. In addition, $n = 3$ [22] (with the effect of surrounding dipoles replaced by a mean field) and $n = 4$ [23] state models have been investigated. We shall not discuss these and other dipole models in depth because this has recently been done by Marshall and Conway [24], and by Marshall [25] in great detail.

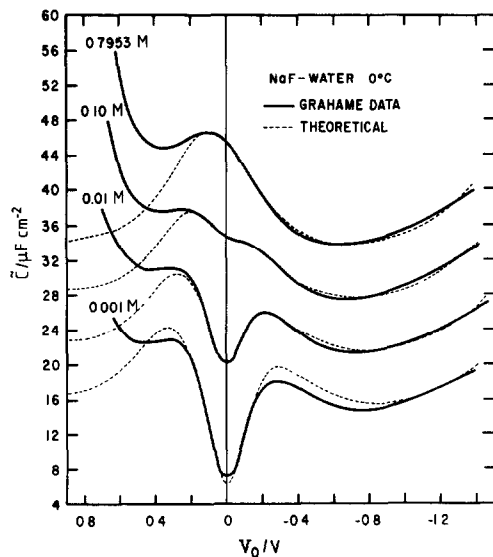


Fig. 6. Comparison of Grahame 0°C C_T results with continuum theory (reprinted with permission [5,14]).

One of the major problems in many of these studies, besides that of determining the most appropriate value of n to use, is how to take dipole-dipole interactions into account properly. One approach, an extension of the $n = \infty$ theory discussed

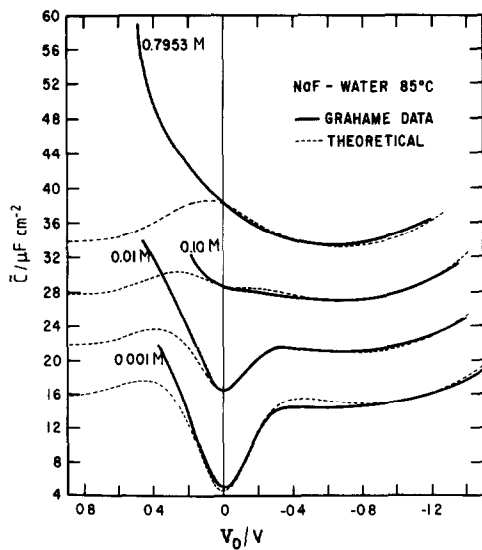


Fig. 7. Comparison of Grahame 85°C C_T results with continuum theory (reprinted with permission [5,14]).

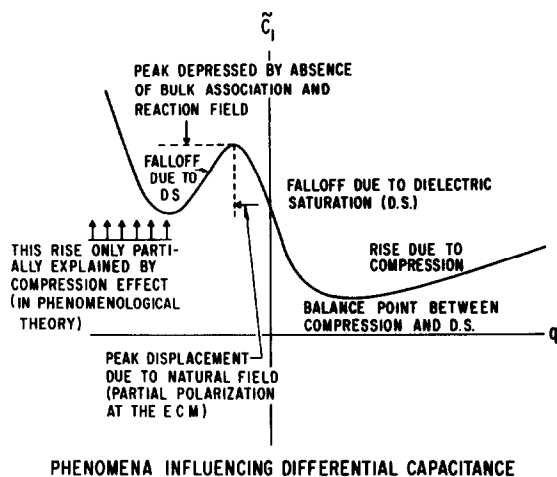


Fig. 8. Summary of main phenomena influencing C_T in the continuum theory [1].

above, includes both induced and permanent dipole moments (no explicit dielectric constant introduced) and treats interactions approximately but self-consistently by means of a modified cutoff disk method (to be discussed below for the specific adsorption case), including some dipole imaging [6,26,27]. Mean field and other approximate statistical mechanical treatments of interaction have been used by some, but Schmickler [28], in connection with a recent investigation of models with different n s and of a cluster model, concluded that “the strength of the dipole–dipole interaction precludes the use of simple approximations like the mean field approximation” [29]. Further, he found, on the basis of an approximate Monte Carlo treatment of a monolayer of point dipoles, that the $n = \infty$ model with exact dipole interactions for nearest neighbors and mean field interactions beyond, was much superior to those with $n = 3$ and $n = \infty$ with more approximate interaction relations [29].

In 1975 Cooper and Harrison [30] pointed out that the $n = 2$ dipole model could lead to non-physical negative differential capacitance values for reasonable values of the relevant parameters of the model. Much attention has been directed since then at this Cooper–Harrison catastrophe (CHC) [31], and numerous papers have been devoted to discussing and even explaining it. It has been ascribed, for example, not to an incorrect method of calculation but instead to the approximation of real molecules as point dipoles [28]. Another recent paper concludes that the CHC is avoided if the dipole–dipole coordination number is greater than 14.5 [32]! Nevertheless, the CHC is a non-problem, a pseudo-catastrophe arising from an error in elementary electrostatics. Again we need not discuss the matter in detail because that has recently been done, for various values of n , by Marshall and Conway [24]. Here it is sufficient to summarize and extend their conclusions somewhat.

These authors have pointed out that the CHC disappears, for all the models

considered, when (i) calculations ensure the continuity of dielectric displacement across the electrode/inner-layer interface; when (ii) dielectric displacement continuity is maintained across the inner-layer/solution interface; and when (iii) continuity of the potential is ensured between the inner layer and the solution. Although Marshall and Conway point out that the $n = \infty$ treatment of Macdonald and Barlow [14] does not involve a CHC because the proper continuities are maintained, they did not mention that this was also the case in even the 1954 phenomenological treatment of the EDL by the present author [13]. The matter may be closed, it is to be hoped for good, with the following quotation from p. 27 of the Marshall thesis [25]: “The importance acquired in the literature by the catastrophe since publication of ref. 16 (the present ref. 30) suggests that Cooper and Harrison and subsequent authors were unaware of the purport of the earlier work of Macdonald and Barlow (present ref. 14)”.

(II.a.2) Specific adsorption

Consider Fig. 2 once more. Since the use of a dielectric constant (a semi-macroscopic concept) at all in a microscopic region is a considerable approximation, it is usually scarcely worthwhile to distinguish between the quantities ϵ_β and ϵ_γ of Fig. 2. If one does not and takes their common value as ϵ_A , then $C_\beta = \epsilon_A/4\pi\beta$ and $C_\gamma = \epsilon_A/4\pi\gamma$. Although these quantities should depend somewhat on σ_m , they are often taken independent of it in specific adsorption calculations. When they are, it turns out that a fully self-consistent expression for the total differential capacitance associated with the Fig. 2 model is possible [16]. Although this treatment has been explicitly developed for the aliovalent ionic single crystal situation (e.g., for AgBr), it applies as well to the liquid electrolyte case with suitable redefinition of the quantities involved [5].

The analysis first yields the more or less conventional expression [33],

$$C_T^{-1} = C_\beta^{-1} + C_\gamma^{-1} + C_{dl}^{-1} + (C_\gamma^{-1} + C_{dl}^{-1})(d\sigma_s/d\sigma_m) \quad (2)$$

which is often presented without the C_{dl}^{-1} terms. Here, $C_{dl} \equiv -d\sigma_d/d\psi_d$. But the ratio $(d\sigma_s/d\sigma_m)$ may be expressed as

$$(d\sigma_s/d\sigma_m) = (C_\beta^{-1} - C_T^{-1})C_A \quad (3)$$

where $C_A \equiv -d\sigma_s/d\psi_s$. The presence of the C_T^{-1} term in eqn. (3) provides a feedback factor. When eqn. (3) is substituted in eqn. (2) and the result solved for C_T^{-1} , one finds that the overall differential capacitance C_T is exactly represented by the simple electrical circuit of Fig. 9, a result necessarily contingent on the applicability of the Fig. 2 model but nevertheless not well known in the electrochemical area. When one assumes that the work of adsorption does not involve the transport of the ion to be adsorbed through the diffuse layer, C_A may be defined as $-d\sigma_s/d(\psi_s - \psi_d)$. One then finds $C_T^{-1} = C_\beta^{-1} + (C_A + C_\gamma)^{-1} + C_{dl}^{-1}/(1 + C_A C_\gamma^{-1})$, a result which does not lead to a simple equivalent circuit made up of capacitors in series and parallel like that of Fig. 9.

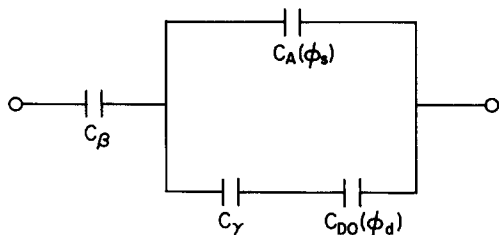


Fig. 9. Exact equivalent circuit for C_T associated with the model of Fig. 2 [16]. Here $\phi \equiv \psi/V_T$, where $V_T \equiv kT/e$, the thermal potential. In addition, $C_{DO} \equiv C_{dl}$.

To apply the Fig. 9 circuit self-consistently, one must also use the simple equations which follow from ordinary electrostatics with continuity of dielectric displacement and relate ϵ_m , σ_s and ψ_m , ψ_s , ψ_d [16]. In addition one must introduce an adsorption isotherm, $\sigma_s(\psi_s)$, which relates the amount of (average) adsorption to the (average) local potential at the IHP and so yields an expression for $C_A(\psi_s)$. Finally, some model of the diffuse layer must be used to provide an expression for the potential-dependent diffuse layer differential capacitance $C_{DO}(\psi_d) \equiv C_{dl}$. Some specific choices for these sub-models will be discussed in the next section. Note that it is unnecessary to iterate to obtain full self-consistency for the Fig. 9 circuit if one considers ψ_d as the known variable [16]. It is worth emphasizing that Fig. 9 shows that it is improper to take C_β and C_γ in series electrically when C_A is non-zero, as has sometimes been suggested. The requirement of self-consistency in the present approach clearly leads to a more complex situation. When an expression for C_{dl} is available, comparison of experimental C_T data with Fig. 9 circuit predictions should allow C_A to be calculated as a function of σ_m or σ_s . Such results, in turn, may then be used to calculate the adsorption isotherm $\sigma_s(\psi_s)$. Finally, recent work shows that when the Fig. 9 circuit is applicable for potential-independent C_β and C_γ , it also applies when these quantities are potential-dependent and are defined as differential capacitances.

(II.b) Discreteness and ion size effects

In this section I shall discuss EDL approaches and models where the discreteness of ions and, later, solvent molecules is recognized and at least partly accounted for. In such treatments the finite size of these entities is not wholly neglected as it is in say the GC model. In the most discrete of the models to be considered, the nm, where the ions and molecules can move freely under the influence of their mutual interactions and a field arising from charge on the electrode, no explicit inner layer needs to be introduced. In the most general treatment, instead of using a separate, often ad hoc, adsorption isotherm, which may or may not be appropriate, the absence or presence of adsorption should be a consequence of the basic general equations governing the ensemble.

(II.b.1) Three-dimensional lattice-gas model

One approximate way to take some account of finite ion size is to require that mobile charges only occupy sites of a three-dimensional lattice whose lattice parameter is determined by the effective diameter (p. 97 of ref. 6) of the ions (usually taken the same for cations and anions). Such lattice-gas models (lgm) have proved useful for liquids even though they involve more order than actually present. Intuitively, one might expect the lattice to approximate the close packing of ions which tends to occur near the electrode in liquid electrolytes at high applied fields and to have little or no effect far from the electrode where charge density is low.

A lgm has been developed and applied primarily to aliovalent alkali halide single crystals [16], a situation for which the lattice assumption is fully warranted. It involved "non-interacting" lattice gas statistics for the mobile charges. Thus the only interactions between them arise from the constraint that they can occupy only available sites. Each site is therefore either "empty" (filled with a solvent molecule) or is occupied by a positive or negative entity. Except for this constraint, this lgm is essentially a cm since it involves ϵ_B , rather than the discrete electrical effects of the individual solvent molecules, except in the inner region (see Figs. 2 and 9). It can be applied as an approximate model for the EDL even for liquid electrolytes and includes the possibility of specific adsorption arising as an integral part of the analysis. For comparison, note that the CG theory is that of an ideal-gas model (igm), one involving non-interacting charge carriers of infinitesimal size.

It is interesting to note that the lattice gas statistics of the above treatment lead to an expression for average ionic concentration as a function of the average potential at the point in question which may be identified as a three-dimensional Langmuir isotherm [16]. In addition, the analysis assumes that there are a limited number of single-occupancy surface lattice sites available for ions (specific adsorption sites in the liquid electrolyte situation). Then Gibbs free energy minimization yields an adsorption isotherm of exactly the form of the usual two-dimensional Langmuir isotherm. Under reasonable conditions the dependence of σ_s on ψ_s is of the tanh form, essentially the same form as the polarization charge of the two-state model of point dipoles in the inner layer [24]. Thus, the possibility of confusion should not be overlooked. When the lgm results are used to quantify the elements in the Fig. 9 circuit, C_T may be readily calculated. Thus far, however, calculations and results have been presented [16] which are most appropriate for the single crystal case rather than for aqueous electrolytes. It is worth mentioning, however, that without the separate introduction of a natural field, adsorption is not zero at the pzc and a large region is found where σ_s depends linearly on σ_m , as illustrated in Fig. 10.

(II.b.2) Specific adsorption and the modified cutoff disk method

Thus far we have considered ψ_s , the potential which is associated with specific adsorption at the IHP, to be an averaged, local potential. But it has long been recognized (e.g., refs. 34 and 35) that the actual potential which "produces" adsorption is that at the adsorption position in the absence of the adion itself, a micropotential. A great deal of effort has been devoted to calculations of such

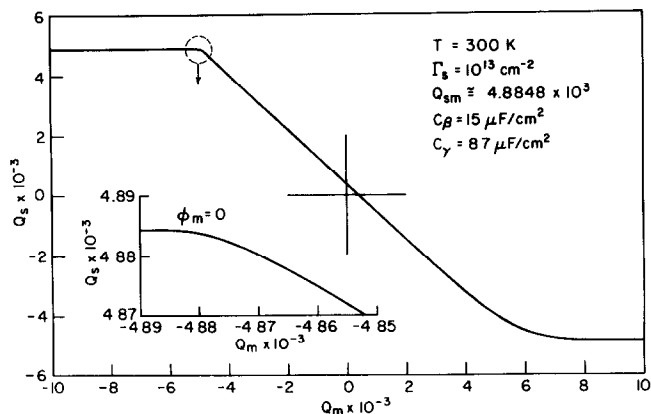


Fig. 10. Adsorption isotherm for the lgm; Q_s and Q_m are normalized adsorbed charge and charge on the electrode, respectively [16].

quantities as the micropotential, which are associated with charge discreteness, and the area was reviewed through 1966 in ref. 6. More recent work, particularly on specific adsorption, has been discussed recently by Marshall [25]. When the micropotential, rather than the average potential, is used in an adsorption isotherm such as that discussed above, more realistic results will be obtained. One approximate method of micropotential calculation is the use of the Grahame cutoff disk model (gcdm [36]). Charge adsorbed in the IHP is taken averaged, and a disk of radius r_0 , centered at the adsorption position, is taken free of charge, with r_0 determined by charge conservation. The potential at the center of the disk, an approximation for the micropotential, is then relatively readily calculated, even in the presence of single or infinite imaging.

In the more accurate modified cutoff disk method (mcdm [6,27]), the radius of the disk, r_b , is taken to be a more complicated function of adion number density than in the Grahame case. This allows the approach to yield virtually exact micropotential estimates in the two limiting occupancy regions: that where the adions are sufficiently close to each other that Coulomb repulsion ensures that they lie on a hexagonal array, and that where they are so far away from each other on the average that they may be taken as moving independently and are randomly ordered. Thus tedious lattice sum calculations are avoided.

Results for the normalized mcdm radius, $R_b \equiv r_b/\beta$, vs. the normalized hexagonal array nearest neighbor distance, $R_1 \equiv r_1/\beta$, are presented in Fig. 11 for a particular situation. Since no accurate values of R_b are available in the transition region, several empirical bridging curves are shown; of these, curve *b* is probably most appropriate. Future Monte Carlo studies should allow this part of the curve to be well determined. Note that R_b is temperature dependent; in particular, the R_1 values where the transition region begins and ends depend directly on temperature. The dashed line in the figure, the normalized Grahame prediction, is clearly much

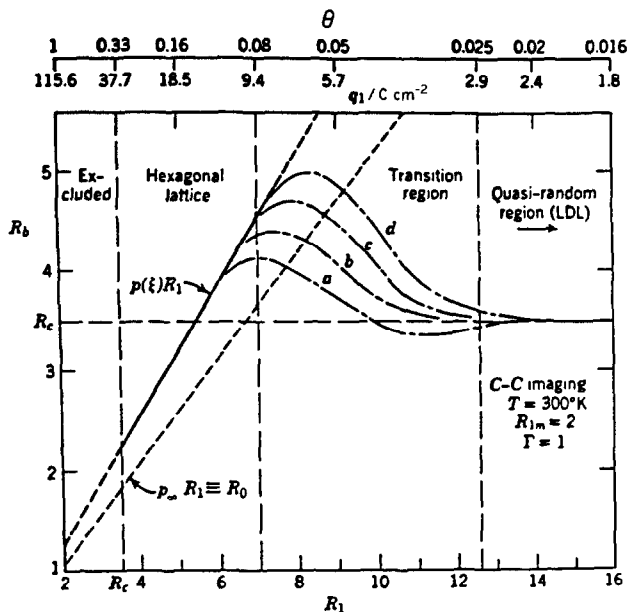


Fig. 11. Normalized disk radius, R_b , vs. normalized hexagonal lattice spacing, R_1 , for the modified cutoff disk method. Quantities normalized with the distance β (reprinted by permission of John Wiley and Sons, Inc., copyright © 1967 [6]).

less accurate over the available occupancy region than is that of the mcdm. In recent work on the depolarization of adions arising from their neighbors in a plane [37], the gcdm and lattice sum calculations were separately employed to calculate the micropotential instead of using the simpler mcdm approach.

A serious, largely unsolved problem with usual micropotential calculations in the liquid electrolyte area, including those discussed above, is that it is likely to be a poor approximation to represent the solvent molecules in the neighborhood of adions by just a small field-independent dielectric constant, as above, or even by one which decreases with increasing field. The discrete effects and interactions of both adions and solvent molecules in the inner layer should be simultaneously accounted for, with the molecules at least replaced by hard spheres with permanent embedded point dipoles. An approximate mean field calculation of these effects has been carried out recently by Marshall [25], but the results are unsatisfactory, probably in part because of the inadequacy of the mean field approach. Alternatively, some recent work [38,39] on adsorption isotherms has considered dipole effects and adion interactions more from a continuum standpoint. Incidentally, when the adsorption capacitance C_A is defined as $-\delta\sigma_s/d\psi_i$, where ψ_i , the micropotential, is used in place of the average potential ψ_s , the simple Fig. 9 circuit for C_T still applies, with an effective C_A , when the micropotential parameter λ [6] is taken charge independent.

(II.b.3) Discrete primitive model and electron overlap

In this model the ions are represented by charged hard spheres, the solvent as a medium of uniform dielectric constant ϵ_s , and no inner layer is included. The model thus applies only to the diffuse region of the EDL and is more applicable to fused salts, and possibly solids, than to liquid electrolytes. It has been analyzed in recent years through the use of sophisticated statistical mechanics, often involving complicated, though approximate, integral equations in an attempt to account properly for ion-ion interactions. Recent reviews [8] contain summaries of the approaches and references to much of the work in the field. Unfortunately, because of the complexities of the analysis it has generally been impossible to extend results to the region of large electrode charges and applied potentials. The results of the various theories, all using $\epsilon_s = \epsilon_B$ (taken as 78.5 for water at $T = 298$ K), have been compared with Monte Carlo simulations of Torrie and Valleau [40,41]. These comparisons show that while the gcm is relatively poor, good fitting is found for several of the statistical theories, at least over the limited range for which they yield results. Henderson [8] has pointed out, however, that the present model is mainly of theoretical interest because it is insufficiently realistic.

Recently the quantum mechanical nature of the conductive properties of the metal electrode used in EDL experiments has been recognized and taken into account explicitly [8,19,42,43]. The main effect is electron spillover from the metal into the solution, with such spillover being slightly sensitive to the direction of the field in the region next to the electrode [43]. Because of spillover the effective ESP lies in front of, rather than behind, the physical surface of the electrode. For the inner layer picture, such overlap thus causes the thickness correction, d_p of Section II.a, to be negative rather than positive. The theory is complicated, approximate, and involves several parameters, but its results indeed lead to better agreement with experiment than if d_p is taken zero or positive [8].

(II.b.4) Modified lattice-gas model

A model also applicable only to the diffuse region, like that above, is obtained if we add mean field corrections to the diffuse region solution obtained from the lattice-gas model of Section II.b.1. To do so, we add pair interaction energy terms of Coulomb form to the free energy of the lattice gas system and then minimize [44–46]. These terms involve a dimensionless parameter α which measures the strength of the interaction. It is positive for repulsion between charges of the same sign, and its presence renders charge calculations implicit, requiring iterative solution. Figure 12 shows results for several values of α compared to both the gcm and the Monte Carlo results mentioned above. The dotted vertical line marks the limit over which the dpm discussed above has been compared for the same one molar situation. Clearly, this model has not been tested against the Monte Carlo results over much of their range. On the other hand, the present model, marked LLGM in the figure but designated mlgm hereafter, yields excellent agreement over the full available range when $\alpha = -3$, agreement to better than a single standard deviation of the simulation results. The mlgm is also far simpler to use than any of the

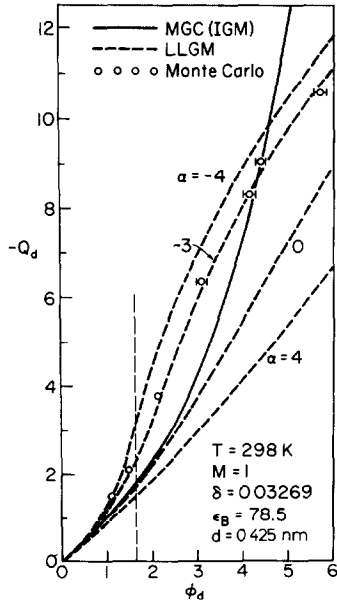


Fig. 12. Normalized diffuse double layer charge density vs. the normalized potential difference across it [44]. Potential normalized with V_T .

free-ion statistical approaches of the dpm, yet applies even up to the saturation region. As Henderson [8] has remarked, finite-size ion packing effects become important even when the packing is only about a tenth that of a close-packed monolayer (see, e.g., the dependence on θ in the present Fig. 11). Although the mlgm is more averaged than the dpm, it seems much superior for use in the diffuse region if one assumes that the Monte Carlo results in fact well represent the actual situation there.

The magnitude of α found above is far smaller than that for full Coulomb interaction because most of the necessary Coulomb interactions have already been implicitly incorporated in the solution through the local satisfaction of Poisson's equation. The negative sign of α implies, in fact, that Poisson's equation overcompensates the interaction slightly, requiring the addition of a small residual attraction between ions of like sign [44]. Fits have also been carried out between the present model and Monte Carlo results for $M = 0.1$ and 0.01 as well as the present $M = 1$. Although there are fewer simulation results available for the lower concentrations, good fits were also obtained for these concentrations with $\alpha = -3$, independent of concentration as expected from mean field theory, but such fits required that the basic lattice spacing parameter of the model increase slightly with decreasing concentration. These results thus suggest that the approximation of a fluid situation by a lattice model is improved by an increase in lattice step size at low concentrations.

(II.b.5) Non-primitive model

In this fully discrete model (the nm), the ions are taken as charged hard spheres and the solvent molecules also as hard spheres but with embedded permanent point dipoles. The dipoles are assumed to be fully orientatable, the $n = \infty$ situation. No explicit inner layer region is included, or needs to be included, in this model. Unfortunately, no simulation results for this system exist, probably because of the strong interactions present which are not reduced by the factor $1/\epsilon_s$ as they are in the pm. Although this is possibly the most realistic model thus far considered for the EDL, it is still appreciably idealized. In particular, the actual steric interactions in a real system are more complex than those represented by hard spheres; point rather than more realistic finite-length dipoles or multipoles are considered; no induced polarization of molecules and ions is included; specific adsorption is not included; and no imaging is present.

Recent work on the nm has been discussed and summarized by Henderson [8]. The statistical mechanical problem presented by this model is very difficult, even when all interactions are not included and a linear approximation is employed. Even under these conditions, Henderson [8] has stated that the solution is "hopelessly implicit". Thus far, results have only been obtained for low concentrations at the pzc. These results are in good agreement with experiment at this point when a negative d_p , ascribed to electron spillover, is included. In view of the complexity of the model, its remaining idealizations, and the presence of very few disposable parameters, this is indeed a substantial achievement.

(II.b.6) Some layered lattice-gas models

The lg and mlg models are pertinent only for single crystals when there are many crystal planes contained in a Debye length, L_D . Only then is it appropriate to include the averaging over microscopic regions implicit in the use of a differential equation such as the Poisson equation, a continuum approach. Similarly, for a liquid electrolyte these models will only be reasonable approximations when L_D is much larger than the ionic diameter, or lattice spacing when the lattice gas approach is used. But this condition is not necessarily satisfied for the local Debye length in a high-field region near an electrode where a very high concentration of ions of one sign is possible. It then becomes appropriate to replace differentials by differences and differential equations by difference equations, thus taking discreteness more into account.

The above considerations led to the development of layered lattice gas models (11gm [45,47–50]) for the EDL. Again a three-dimensional lattice, lattice spacing a , is employed with its (100) plane parallel to the electrode. Then the electrical effects of each plane in the lattice parallel to the electrode are considered individually, with appropriate electrical continuity relations maintained from plane to plane. Each plane is thus treated as a two-dimensional lattice gas, and electrical conditions in every plane are closely coupled in an overall self-consistent way to those in adjoining planes (and so to those in all planes). Let $\Delta \equiv a/L_D$, where L_D is the bulk Debye length. It was found that for $\Delta > 0.01$, significant differences began to

appear between the lg and llg models. Of course as Δ approaches zero the two models approach full equality. In actual calculations with the llgm, double, nested iterations are needed to achieve self consistency. First, iteration is needed for each individual layer to find its self-consistent average charge and potential; then an overall iteration is carried out to ensure electroneutrality for the entire system. We generally extended this iteration until the local potential for the i th layer was less than 10^{-6} of the applied electrode potential, yielding a very good approximation to electroneutrality. Incidentally, an analytic solution with no iteration necessary applies in the weak field limit.

Three different llgms have been developed. The first and simplest involved only ions in each plane, with the solvent represented by ϵ_s in the usual pm fashion. It was found that this model could fit the Monte Carlo diffuse layer simulation results very well at all three available molarities without the need for the mean-field correction of the mlgm. Unfortunately, however, the parameters derived from the fits were somewhat anomalous [45]. The second llgm model [47,48] represented an initial attempt to take the dielectric effects of the solvent molecules into account in a more realistic way. Their polarizability was represented by a small dielectric constant ϵ_∞ , taken as 6 for water, and the effect of their permanent dipole moments by an approximate continuum treatment of saturable finite-length dipoles. A statistical mechanical free energy minimization was carried out to determine the (average) occupancy of each lattice site by a positive or negative ion or by a molecule. Thus while the first llgm was primitive, the second represented a step toward a non-primitive model treatment.

Although no explicit charge-free layer of solvent molecules is necessarily present in any of the llgms, they nevertheless inherently involve a small charge-free inner layer since the first plane of the lattice next to the electrode is a distance of r_i ($= a/2$), or $r_e \equiv r_i + d_p$, away from the ESP. In this sense they are thus approximate theories of the entire EDL, not just the diffuse layer alone. It was found [48], however, that the second llgm nevertheless yielded appreciably too high C_T values at the pzc, as compared to experimental results [17,18], when the separation r_i was employed. Even worse results would be obtained if r_e were to be used with d_p negative because of electron spillover. On the other hand, excellent agreement with the data was found if d_p was taken as 2.9 pm (with $\epsilon_\infty = 1$), thus adding to the effective thickness of the inner layer. It is not entirely clear why additional thickness should be needed, but the causes are likely to be one or all of the following: intrinsic problems with the lattice-gas approximation, inadequate treatment of the effects of the multipole moments of the solvent molecules, and, most important, the presence of some solvated molecules between the ions nearest the electrode and the electrode itself.

The third llgm [49,50] was developed to eliminate some of the approximations inherent in the second model. Solvent polarizability was handled either by the introduction of ϵ_∞ or by the more discrete alternative of setting $\epsilon_\infty = 1$ and taking the polarizability of the individual solvent molecules non-zero. The effects of the permanent multipole moments of the solvent molecules were approximated by

actual orientatable finite-length dipoles with $n = \infty$ and some interaction effects included, a discrete, and considerably more complicated, treatment. Again an inner region different from the rest of the material was needed for agreement with experiment at the pzc. Here, however, in keeping with the more microscopic and discrete character of the approach, we took the first layer of the llgm as having finite-length dipoles with the bare dipole moment of water, rather than a higher value which would help account for cooperative effects and is used in the other planes to yield the proper dielectric properties of the bulk. Little difference in results was found at the pzc whether we took this first layer charge-free or allowed ions to compete with dipoles for site occupation.

One of the most interesting results of this third llgm was that very little effective dielectric saturation is predicted as compared to more conventional treatments using continuum or point dipole approaches. In particular, it turns out that for the present finite-length dipole case it takes a field ten times or more higher to produce the same amount of saturation as that obtained with a smaller field in conventional approaches. To the degree that these results are applicable to real situations, they suggest that little dielectric saturation will occur in actual situations in the region near the electrode and that it can be completely neglected elsewhere.

Next it is of interest to present results of this treatment for the occupancy and saturation of the first layer of the full many-layer llgm. Figure 13 shows, as a function of normalized applied potential and for two different molarities, how the occupancy of dipoles decreases and that of ions increases as the potential increases. Figure 14 shows, for a concentration of 1 mol l^{-1} and with a smaller permanent dipole moment than that used in Fig. 13, how the amount of saturation depends on

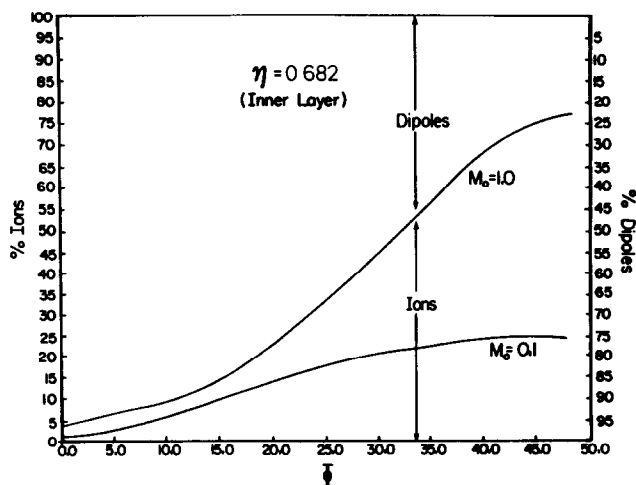


Fig. 13. Competition for site occupancy following from the third layered lattice gas model [50]. Φ is the potential difference between the electrode and infinity normalized with V_T .

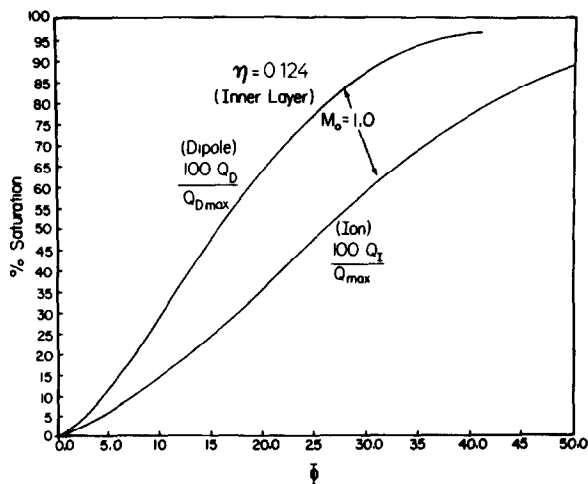


Fig. 14. Ion and finite-length dipole saturation percentages as functions of Φ [50].

potential for both the competing ions and the dipoles. Here Q_D , the effective normalized dipole charge, measures the effects of both orientation and dipole concentration, and Q_{max} is the maximum possible normalized charge density. For the experimental range of normalized potential, up to 10 or 20, neither the ions nor the dipoles are close to their maximum saturated values. Finally, it should be mentioned that several of the present llg models have recently been compared [51] with a cutoff disk non-lattice-gas theory [52], a theory which attempts to unify inner layer and diffuse layer treatments. The third llgm discussed above is more discrete and likely to be more accurate than such a cutoff disk theory, and, in addition, it allows calculations to be made far away from the pzc, unlike the complicated integral-equation non-primitive models discussed in Section II.b.5.

(II.b.7) Conclusions

Now that the EDL territory has been covered in a bird's-eye view, what conclusions can we draw? First, it seems apparent that the integral-equation statistical treatments are too complicated and too limited in applicable charge or p.d. range to be of practical usefulness. Second, the results discussed suggest that in all real situations the present mlgm is entirely adequate to describe the diffuse layer over the entire available experimental p.d. range. Further, this lattice gas model is relatively simple mathematically and can be expressed in terms of an implicit closed-form equation for local charge density. But there are still serious outstanding problems for the inner layer, the first layer of molecules and possibly ions next to the electrode.

Results obtained by many workers in this field allow us to reach, with considerable certainty, the following negative conclusions. The approximation of taking

solvent molecules as point dipoles with n states (n arbitrary) is inadequate. The use of even finite-length dipoles is often inadequate, and higher multipoles are needed. Mean-field or quasi-chemical approximate treatments of lateral interaction of solvent molecules are inadequate. A discrete treatment involving both near and far interactions is needed. Until the interaction problem can be better solved, it seems hardly worthwhile to devote much effort to distinguishing between two-, three-, and ∞ -state models with the solvent molecules taken as point dipoles. The situation is even worse in the presence of specific adsorption, and perhaps Monte Carlo treatments give most hope for the future.

ACRONYM DEFINITIONS

cm	continuum model
cpm	continuum primitive model
dm	discrete model
dpm	discrete primitive model
gcdm	Grahame cutoff disk model
igm	ideal-gas model
lgm	lattice-gas model
llgm	layer lattice-gas model
mlgm	modified lattice-gas model
mcdm	modified cutoff disk model
nm	non-primitive model
CHC	Cooper–Harrison catastrophe
EDL	electrical double layer
ESP	electrode surface plane
GC	Gouy–Chapman
GCS	Gouy–Chapman–Stern
IHP	inner Helmholtz plane
OHP	outer Helmholtz plane

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