

THE JOURNAL OF
PHYSICAL CHEMISTRY

Registered in U. S. Patent Office © Copyright, 1964, by the American Chemical Society

VOLUME 68, NUMBER 10 OCTOBER 15, 1964

Electric Monopole and Dipole Discreteness Effects in Adsorption

by J. Ross Macdonald and C. A. Barlow, Jr.

Central Research Laboratories, Texas Instruments Incorporated, Dallas, Texas 75222
(Received July 18, 1964)

Various consequences of element discreteness upon the electrical characteristics of adsorbed systems of monopoles and dipoles are discussed and methods for determining exact local potentials and fields in such systems are outlined in terms suitably general for wide application.

In the present paper we shall summarize some of the discreteness-of-charge effects accompanying adsorption and also describe some recent techniques for making exact discreteness-of-charge calculations possible. Before discussing any particular system, it is well to recognize that discreteness may produce a number of different effects: In particular, a given discrete array of monopoles or dipoles produces a potential which at almost any point differs from that produced by the continuous distribution of charges obtained by smearing the discrete entities over their plane. On the other hand, the potential averaged over a plane parallel to that of the array is equivalent to that obtained by smearing the discrete distribution in its plane. We see, therefore, that any property which depends on a more detailed behavior of the potential than merely the average will directly manifest discreteness effects. Examples of such properties relate to basic gas or liquid adsorption theory,¹⁻¹⁴ thermionic¹⁴ and high field emission¹⁵ characteristics, and electrode electrochemical kinetic properties.¹⁶⁻¹⁸ Less obvious is the fact that discreteness will also indirectly influence the average potential. The manner in which this comes about is as follows. If the discrete array of elements is polarizable, either through orientation of permanent dipoles or

creation of induced dipoles, the polarization depends on the local field acting to polarize the entity; this local field is the sum of the applied field and that arising from

- (1) J. R. Macdonald and C. A. Barlow, Jr., Proceedings of the 1st Australian Conference on Electrochemistry, Sydney, Australia, Feb., 1963, to be published.
- (2) A. N. Frumkin, *Phys. Z. Sowjetunion*, **4**, 256 (1933).
- (3) O. Esin and B. Markov, *Zh. Fiz. Khim.*, **13**, 318 (1939); *Acta Fiz. Khim. URSS*, **10**, 353 (1939).
- (4) C. A. Barlow, Jr., and J. R. Macdonald, *J. Chem. Phys.*, **40**, 1535 (1964).
- (5) O. Esin and V. Shikov, *Zh. Fiz. Khim.*, **17**, 236 (1943).
- (6) D. C. Grahame, *Z. Electrochem.*, **62**, 264 (1958).
- (7) S. Levine, G. M. Bell, and D. Calvert, *Can. J. Chem.*, **40**, 518 (1962).
- (8) B. V. Ershler, *Zh. Fiz. Khim.*, **20**, 679 (1946).
- (9) V. G. Levich, V. A. Kir'yanov, and V. S. Krylov, *Dokl. Akad. Nauk SSSR*, **135**, 1193 (1960); V. S. Krylov, *ibid.*, **144**, 356 (1962).
- (10) R. J. Watts-Tobin, *Phil. Mag.*, **6**, 133 (1961).
- (11) N. F. Mott and R. J. Watts-Tobin, *Electrochim. Acta*, **4**, 79 (1961).
- (12) W. A. Steele and M. Ross, *J. Chem. Phys.*, **35**, 850 (1961).
- (13) W. Anderson and R. Parsons, *Proc. 2nd Intern. Congr. Surface Activity*, **3**, 450 (1957).
- (14) A. J. Kennedy, *Advan. Energy Conversion*, **3**, 207 (1963).
- (15) R. Gomer, *J. Chem. Phys.*, **21**, 1869 (1953).
- (16) A. Aramata and P. Delahay, *J. Phys. Chem.*, **68**, 880 (1964).

the elements themselves. Since the latter contribution differs from the smeared (average) field, the net polarization and hence the effective dielectric constant of the array is a further property which could have been listed above as evincing discreteness-of-charge effects. The departure of the dielectric constant from the bulk value, which can be properly calculated only by taking full account of discreteness effects, has consequences¹⁹⁻²⁴ on the dependence of contact potentials or work functions upon adsorption and influences the differential capacitance of the electrical double layer in an electrolytic solution.^{1,10,25-28}

In the present paper it is assumed that the adsorbed particles form a hexagonal array of spacing r_1 lying at the inner Helmholtz plane (IHP) and that one or the other of the following idealized situations prevails. Either there exist two equipotential planes, one on either side of the IHP which, like a hall of mirrors, produces an infinite set of images, or else one such plane exists (taken here to be the plane adsorbing electrode) and acts to produce single images of the adsorbed entities. In the former situation, appropriate to some degree to adsorption from electrolytes, one imaging plane is the electrode and the other is the outer Helmholtz plane (OHP), the plane of closest approach and maximum concentration for unadsorbed ions in the diffuse or Gouy layer^{1,25,26,29-36} of the electrolyte. The inner or Stern layer^{1,25,26,37} between the electrode and the OHP will be the primary region of interest in our discussion of the electrical double-layer problem, and for "unadsorbed electrolytes" will contain a monolayer of adsorbed solvent molecules taken here to be water.^{1,25,26}

In earlier papers,^{1,25,26} an effort was made to explain the differential capacitance data of Grahame³⁸ for aqueous NaF solutions at various temperatures, concentrations, and electrode charges. It was found that many of the features of the experimentally determined inner-layer differential capacitance could be explained without recourse to discreteness effects. In particular, the displacement of the point of maximum inner layer capacitance from the electrocapillary maximum potential (e.c.m.) could be ascribed to a natural orienting field at the electrode, of order 10^6 to 10^7 v./cm., which acts to align the water dipoles somewhat with the hydrogen toward the electrode. The fall-off of capacitance on either side of this maximum was accounted for by including dielectric saturation of the inner layer, and the eventual rise in capacitance at potentials further from the e.c.m. was explained by the compression of the inner layer under the large fields present therein. The actual values of capacitance were generally in excellent agreement with experiment over the varying potentials, temperatures, and concentrations, and, pro-

vided lack of association between water molecules was assumed, all best-fit parameters such as compressibility, thickness, dielectric saturation constant, etc., were in agreement with those to be expected based on bulk water values. In spite of the general success of this work, one feature of the data could not be explained: the rapidity of the final rise in capacitance at substantial anodic voltages.^{38,39} This rise has been ascribed by various authors to adsorption, perhaps of OH^- ,⁴⁰ perhaps of F^- ,²⁶ perhaps of electrode "ad-atoms."^{10,11} Parsons¹⁸ suggests that an increased compressibility may be responsible. Although these explanations are possibly correct, the situation is far from clear. The point is that a reasonable fit to Grahame's data may be obtained without assuming adsorption other than the initial water monolayer simply by properly taking discreteness-of-charge into account and its effect upon the inner-layer dielectric constant.^{1,41}

The procedure for obtaining the effective dielectric constant is roughly the following:

-
- (17) A. N. Frumkin, *J. Electrochem. Soc.*, **107**, 461 (1960).
 - (18) R. Parsons, "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, P. Delahay, Ed., Interscience, London, 1961.
 - (19) J. R. Macdonald and C. A. Barlow, Jr., *J. Chem. Phys.*, **39**, 412 (1963).
 - (20) J. K. Roberts, "Some Problems of Adsorption," Cambridge University Press, London, 1939.
 - (21) A. R. Miller, *Proc. Cambridge Phil. Soc.*, **42**, 292 (1946); "The Adsorption of Gases on Solids," Cambridge University Press, Cambridge, 1949, pp. 112, 113.
 - (22) J. H. de Boer, *Advan. Catalysis*, **8**, 118 (1956).
 - (23) I. Higuchi, T. Ree, and H. Eyring, *J. Am. Chem. Soc.*, **77**, 4969 (1955).
 - (24) G. E. Moore and H. W. Allison, *J. Chem. Phys.*, **23**, 1609 (1955).
 - (25) J. R. Macdonald, *ibid.*, **22**, 1857 (1954).
 - (26) J. R. Macdonald and C. A. Barlow, Jr., *ibid.*, **36**, 3062 (1962).
 - (27) R. Hansen, D. Kelsh, and D. H. Grantham, *J. Phys. Chem.*, **67**, 2316 (1963).
 - (28) N. F. Mott, R. Parsons, and R. J. Watts-Tobin, *Phil. Mag.*, **7**, 483 (1962).
 - (29) G. Gouy, *J. Phys.*, **9**, 457 (1910).
 - (30) D. L. Chapman, *Phil. Mag.*, **25**, 475 (1913).
 - (31) R. H. Fowler, "Statistical Mechanics," 1st Ed., Cambridge University Press, London, 1929, pp. 282, 283.
 - (32) H. Müller, *Cold Spring Harbor Symp. Quant. Biol.*, **1**, 1 (1933).
 - (33) J. R. Macdonald and M. K. Brachman, *J. Chem. Phys.*, **22**, 1314 (1954).
 - (34) H. S. Frank and P. T. Thompson, *ibid.*, **31**, 1086 (1959).
 - (35) M. J. Sparnaay, *Rec. trav. chim.*, **77**, 872 (1958).
 - (36) H. Brodowsky and H. Strehlow, *Z. Elektrochem.*, **63**, 262 (1959).
 - (37) O. Stern, *ibid.*, **30**, 508 (1924).
 - (38) D. C. Grahame, *J. Am. Chem. Soc.*, **76**, 4819 (1954); **79**, 2093 (1957); **59**, 740 (1955).
 - (39) M. J. Austin and R. Parsons, *Proc. Chem. Soc.*, 239 (1961).
 - (40) N. Hackerman and P. V. Popat, "Capacity of the Electrical Double Layer and Adsorption at Polarized Pt Electrodes," Technical Report to the Office of Naval Research, 1958.
 - (41) J. R. Macdonald and C. A. Barlow, Jr., to be published.

1. Replace all permanent dipoles by their time averages, $\langle \mu \rangle$.
2. Find the local electric field \mathcal{E} at the dipole sites arising from all other dipoles and induced polarization, the charges on the electrode, and the natural field.
3. Using an expression such as a Langevin function, obtain an implicit equation for $\langle \mu(\mathcal{E}) \rangle$.
4. Write the electronic polarization \mathcal{P}_1 in terms of the local field.
5. Combine all previous steps to find the self-consistent values of \mathcal{P}_1 , \mathcal{E} , and $\langle \mu \rangle$.
6. Express the final result in terms of an effective dielectric constant ϵ_{eff} .

If this program is carried out one obtains¹⁹

$$\mathcal{E} = \epsilon_{\text{eff}}^{-1} \{ 4\pi q - (3/4)^{3/4} \sigma N^{3/2} \langle \mu(\mathcal{E}) \rangle \}$$

where $\epsilon_{\text{eff}} \equiv 1 + (3/4)^{3/4} \sigma \alpha d N^{1/2}$, $q \equiv$ electrode charge; $\alpha \equiv$ electronic polarizability, $\sigma \equiv 11.034$ for a hexagonal array, $d \equiv$ inner-layer thickness, and $N \equiv$ surface density of adsorbed particles. This equation has been solved numerically and, without attempting detailed fitting, leads to the qualitative agreement with Grahame's data mentioned before.

The same procedure may be used to determine the work function change arising from adsorption of ions in the single-imaging situation, provided one approximates the ion-image combination as an ideal dipole. Again, if one carries through the calculation, qualitative agreement with experiment is obtained for coverages θ sufficiently small (≤ 1) that such quantum effects as energy banding may be ignored. The detailed calculation which appears elsewhere¹⁹ leads, under appropriate conditions, to the approximate result

$$\frac{\Delta V(\theta)}{\Delta V(1)} \cong \theta(1 - A)^{-1}(1 - \theta A)$$

where $\Delta V \equiv$ work function change, $\theta \equiv$ fractional coverage of surface by adions ($\theta = 1$ corresponds to a monolayer), $A \equiv 4\pi\alpha N_s/d_1$, $N_s \equiv$ maximum surface density of adions ($\theta = 1$), and $d_1 \equiv$ distance between electrode and adion centroid. For certain values of A the resulting behavior of $\Delta V(\theta)$ exhibits a maximum in the range $0 < \theta < 1$.

In order to calculate exact potentials and fields for discrete arrays, it is necessary to obtain somehow the sum of an infinite series of discrete Coulomb terms. This would present no problem were it not for the extraordinarily slow convergence encountered in either single or infinite image situations. The practical difficulties of obtaining exact results have led several authors^{7,10,11,28} to seek approximate expressions, the accuracy of which is unfortunately not always particularly good; the present authors have proceeded in the other direction,

to obtain more complicated but more rapidly convergent forms for the exact quantities. Comparison of the exact with various approximate results is published elsewhere.^{4,42} The emphasis here will be in outlining the methods, which have been used before in different contexts and are applicable to a wide class of problems.

The simplest method for calculating lattice-sums of Coulomb terms is to multiply each Coulomb term in the series by an exponential convergence factor. Thus, $1/r \rightarrow 1/r \exp(-\delta r)$. The series is then evaluated for several values of δ and an extrapolation performed to ascertain the value for $\delta = 0$. Remark that a powerful method, the ϵ -algorithm,⁴³⁻⁴⁵ exists for performing this extrapolation which is quite accurate and is discussed elsewhere.⁴⁵ The disadvantages of the above δ -method are that several calculations are necessary using different values for δ , some of which (near $\delta = 0$) are not very rapidly convergent; the closer one approaches in the computations to $\delta = 0$, the greater is the final accuracy but the longer is the required computer time. Furthermore, the requirement of a final extrapolation must be regarded as an additional disadvantage. Accordingly, this method has been used by the present authors primarily as a check on other methods or as the technique employed when others are unavailable.

A generally more satisfactory technique^{4,46,47} is schematically described below for the three-dimensional (infinite-imaging) summation.

1. First write the sum to be evaluated, $\sum_k f(\mathbf{R}_k) \equiv S$, as $S = \int d^3R f(\mathbf{R}) \sum_k \delta(\mathbf{R} - \mathbf{R}_k)$, where \mathbf{R}_k are the lattice points and $\delta(\mathbf{x})$ is the Dirac δ -function.

2. Next write the identity

$$S = \int d^3R \sum_k f(\mathbf{R}) \Phi(\alpha \mathbf{R}) \delta(\mathbf{R} - \mathbf{R}_k) + \int d^3R \sum_k f(\mathbf{R}) \{ 1 - \Phi(\alpha \mathbf{R}) \} \delta(\mathbf{R} - \mathbf{R}_k) \equiv S_1(\alpha) + S_2(\alpha)$$

where Φ is an arbitrary function which will be chosen conveniently and α is a parameter which also will be chosen conveniently. Note that $\partial S / \partial \alpha = 0$.

3. Writing the Fourier transform of $\{ f(\mathbf{R}) \Phi(\alpha \mathbf{R}) \}$ as $G_\alpha(\boldsymbol{\lambda})$ and the Fourier transform of $\sum_k \delta(\mathbf{R} - \mathbf{R}_k)$ as $|\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|^{-1} \sum_k \delta(\boldsymbol{\lambda} - \boldsymbol{\lambda}_k)$ where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the

(42) C. A. Barlow, Jr., and J. R. Macdonald, *J. Chem. Phys.*, to be published.

(43) P. Wynn, *Math Tables Other Aids Computation*, **10**, 91 (1956).

(44) D. Shanks, *J. Math. Phys.*, **34**, 1 (1955).

(45) J. R. Macdonald, *J. Appl. Phys.*, to be published.

(46) F. W. de Wette, *Physica*, **23**, 309 (1957); **24**, 422, 1105 (1958).

(47) P. P. Ewald, *Ann. Phys.*, **54**, 519, 557 (1917).

basic lattice vectors and λ_k are the lattice points of the reciprocal lattice⁴⁶ ($\lambda_k \equiv |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|^{-1} \{k_1 \mathbf{a}_2 \times \mathbf{a}_3 + k_2 \mathbf{a}_3 \times \mathbf{a}_1 + k_3 \mathbf{a}_1 \times \mathbf{a}_2\}$), make use of Parseval's theorem⁴⁸ to obtain

$$S_1 \equiv \int d^3\lambda G_\alpha(\lambda) |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|^{-1} \sum_k \delta(\lambda - \lambda_k) = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|^{-1} \sum_k G_\alpha(\lambda_k)$$

where $G_\alpha(\lambda) \equiv \int d^3R f(\mathbf{R}) \Phi(\mathbf{R}) e^{2\pi i \lambda \cdot \mathbf{R}}$.

4. Choose $1 - \Phi$ to be a function which falls off as its argument increases and hence which speeds the convergence of S_2 .

5. Choose α to minimize the total number of terms required for convergence of S . Large α results in rapid convergence of S_2 but slow convergence of S_1 ; small α interchanges these behaviors. An intermediate value may generally be chosen so as to optimize convergence.

6. Test to see that S remains invariant under changes in α . The above method has proven quite satisfactory, and generally the optimum value of α is of the order $[|\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|]^{-1/3}$ with the required independence of the final result upon α providing a stringent test of the correctness of all computations. The function Φ actually used was the error function⁴⁹ in the work cited.⁴

The final technique⁵⁰ to be described here has proven generally to be the best one for summations occurring in practice. It results in an almost closed form expression for the potentials and fields, with the summations remaining frequently contributing negligible amounts to the final result. The vital steps of the method are sketched below.

1. Make use of the relation

$$x^{-n} = \frac{1}{\Gamma(n)} \int_0^\infty t^{n-1} e^{-xt} dt$$

to rewrite the terms of the lattice summation.

2. Introduce the substitution

$$\sum_{l=-\infty}^{\infty} \exp\{-(l+a)^2 t\} = (\pi/t)^{1/2} \times \sum_{s=-\infty}^{\infty} \exp\left\{-\frac{\pi^2 s^2}{t}\right\} \cos(2\pi a s)$$

3. Perform the integration using

$$\int_0^\infty t^{n-1/2} \exp\left\{-k^2 t - \frac{\pi^2 s^2}{t}\right\} dt = 2 \left(\frac{\pi |s|}{k}\right)^{n-1/2} K_{n-1/2}(2\pi k |s|)$$

where K is the modified Bessel function.⁴⁹

4. Execute remaining summations taking limits where special values require it.

The foregoing description is in terms sufficiently general to apply to a rather wide class of problems; however, the reader wishing an example of a specific application of the method may find such elsewhere.⁴²

In summary, we have attempted to sketch some of the consequences of discreteness upon the basic electrical properties of adsorbed lattices. Whereas there has been little attempt here to explore all the secondary consequences of such electrical properties upon macroscopic measurables, clearly element discreteness has its impact upon a large number of surface phenomena. It is gratifying that all the methods outlined herein for exactly performing the pertinent calculations have always produced mutually consistent results.

(48) See, for example, P. Franklin, "A Treatise on Advanced Calculus," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 492.

(49) See, for example, "The Bateman Manuscripts," A. Erdélyi, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1954.

(50) B. M. E. van der Hoff and G. C. Benson, *Can. J. Phys.*, **31**, 1087 (1953).