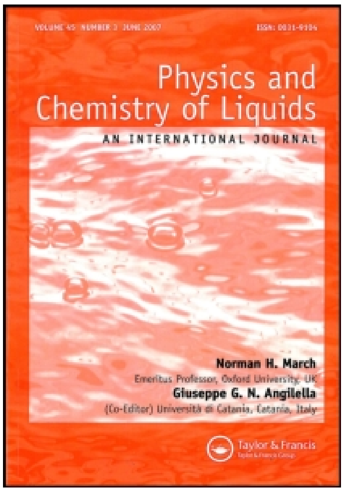

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Structure at Colloid Interfaces†

P. L. DE BRUYN
Gezichtslaan, Bilthoven, Netherlands

The electrical double layer at a solid-liquid interface plays a prominent role in the interpretation of many colloidal phenomena. Adsorption of foreign ions at colloidal particle surfaces is influenced by the surface charge density (σ_0) and the double layer potential (ψ_0). The stability of hydrophobic colloidal solutions is largely controlled by the relative strength of repulsive and attractive (van der Waals) forces which come into play when the double layers of two approaching particles overlap.

The simple Gouy–Chapman model of the double layer features importantly in the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory[1] which is so successful in accounting for the coagulation behaviour of colloids in dilute aqueous solutions containing mono- and divalent ions. This model assumes that, except for differences in ionic concentration all other physical properties (e.g. dielectric constant and viscosity) of the solution are independent of position inside the double layer. Unfortunately, this model, although so elegant and simple in its mathematical formulation, fails to describe the structure of the double layer and the stability of colloids in more concentrated electrolyte solutions or in solutions of highly charged ions.

Over the years considerable effort has been put into the evaluation of the macroscopic properties of the double layer on the solid, silver iodide. This heteroinic solid has become the prototype colloid in most double layer and coagulation investigations. In recent years monodisperse polystyrene latices because of their better defined geometry, have to some extent displaced silver iodide as the model system in fundamental colloidal-stability studies. The characterization of the double layer on spherical latex particles is however not as far advanced as that on silver iodide.

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THE DOUBLE LAYER PROPERTIES OF SILVER IODIDE

The double layer on silver iodide is established by a mechanism which involves the transfer of potential determining (p.d.) ions across the interface. This is in contrast to the polarizable mercury system where charge is transferred, with the aid of an external potentiometer circuit, to but not across the mercury surface. The equilibrium potential difference, ψ_0, across the double layer on AgI may thus be derived by equating the electrochemical potential of the p.d. ion, for example, Ag^+, in the surface to its value in the bulk solution. On introducing the non-operational separation of the electrochemical potential into a chemical and electrical component one finds that

$$\psi_0 = \frac{(\mu^{s0}_{Ag} - \mu^{s}_{Ag})}{F} + \frac{RT}{F} \ln \frac{a_{Ag}}{a^0_{Ag}} \tag{1}$$

where μ^{s0}_{Ag} and μ^{s}_{Ag} refer respectively to the chemical potential of the silver ion at the point of zero charge (pzc) and on a charged surface; a^0_{Hg} is the activity of the p.d. ion in the solution at the pzc and F is the Faraday constant. This expression for μ_0 reduces to the familiar Nernst equation

$$\psi_0 = \frac{2.303RT}{F} (\mathrm{pAg}^0 - \mathrm{pAg}) \tag{2}$$

with $\mathrm{pAg}^0 = -\log a^0_{Ag}$ because silver iodide behaves as a reversible electrode. This transformation to give the Nernst equation also implies that the chemical potential of the silver ion in the surface is not altered by adsorption or desorption of Ag^+. The surface charge density (σ_0) is determined by the difference in the adsorption density (Γ_i) of the positively and negatively charged p.d. ions,

$$\sigma_0 = F(\Gamma_{Ag} - \Gamma_I) \tag{3}$$

It may be measured analytically by potentiometric titrations (with $AgNO_3$ and KI) of a colloidal suspension of silver iodide (2). The differential capacity of the double layer, $C = d\sigma_0/d\psi_0$, may then be derived from the experimental adsorption curves (σ_0 vs ψ_0) at different ionic strengths by using the operational expression

$$C = \frac{F^2}{2.303RT} \cdot \frac{d(\Gamma_{Ag} - \Gamma_I)}{d(\mathrm{pAg}^0 - \mathrm{pAg})} \tag{4}$$

The position of the pzc (pAg^0) is determined by the common intersection point of the adsorption curves measured at different ionic strengths.

Experimental studies conducted with the potentiometric titration technique show that the shape of the adsorption curves for AgI agree remarkably well with similar curves obtained by different experimental methods on Hg. The magnitudes of the double layer parameter σ_0 and C, when compared under identical conditions as regards ionic strength and location relative to the pzc, are also similar. The tacit assumption is made by most colloid chemists that this quantitative agreement in double-layer parameters of mercury and silver iodide may also be assumed to hold for other colloidal systems.

The GCSG (Gouy-Chapman-Stern-Grahame) model of the double layer which was largely developed to explain specific adsorption at the mercury interface has also been adopted as a suitable model for colloidal systems. According to this model the double layer is divided into two regions, an inner Stern layer where specific adsorption occurs and the Gouy-Chapman or diffuse layer occupied by ions which interact only electrostatically with the charged colloid surface. The structure of the solvent adjacent to the solid surface may then be deduced from the electrical properties of the Stern layer.

The GCSG model has obvious deficiencies. One unsatisfactory aspect of this model is the postulated abrupt transition in potential and physical properties of the solvent at the boundary which separates the Stern region (of atomic dimensions) from the diffuse layer. It has however become abundantly clear that one encounters great mathematical and conceptual difficulties when trying to improve this model. As already indicated by Haydon[3] it would be necessary to develop a good statistical theory which gives the potential distribution in the double layer and allows implicitly for the transition from macroscopic features such as dielectric constant to an electrical description of an atomistic discrete model. Such a theory has not been formulated especially, if one demands experimental verification of parameters contained in it. A closer collaboration between the theoretician and the experimentalist than presently exist, is essential. Development of new experimental techniques which allow a more direct measurement of the structural properties of the double layer is also badly needed. Present studies yield macroscopic data which are quite often extrapolated by questionable procedures to yield microscopic details of the inner region of the double layer.

It is nevertheless possible to obtain, by inference, qualitative information about the structural properties of the double layer from precise measurements of macroscopic electrochemical parameters. The structural features of water adjacent to the solid phase must be reflected in changes in the differential double layer capacitance with increasing surface charge. The electrostatic field would be expected to exert an orientating influence on the water dipoles. Information on the orientation and electrostriction of the polar water molecules in the inner reaches of the double layer may also be found through studies of the adsorption of polar organic substances, for example, aliphatic alcohols. These compounds would tend to displace polar water molecules at the interface. By establishing the electrical conditions (ψ_0 and σ_0) under which a maximum in the adsorption of these organics occurs one might be able to predict the preferred orientation for the water dipoles at the surface. Structural information may also be derived from experimental measurements of the dependence of surface charge and capacitance on temperature. With increasing temperature a decrease in specific adsorption of counterious and a greater randomness in the arrangement of the water molecules near the surface are to be expected. With the aid of the Gibbs adsorption equation it should then be possible to derive from the temperature dependence of the surface charge, the changes in interfacial entropy. From a statistical analysis of the entropy data it may be possible to deduce configurational changes at the interface.

Lijklema and associates have conducted experiments of the type suggested in the preceding paragraph with AgI. These investigators concluded from the observed temperature effects on σ_0 at fixed ψ_0[2] and from the adsorption of aliphatic alcohols[5] that at room temperature the water dipoles are most randomly arranged at a slightly negative ($\sim 1 \mu C\ cm^{-2}$) surface. At this value of surface charge a maximum is observed in the adsorption of alcohol. They then proposed that at the pzc water molecules are preferentially oriented with the negative side of the dipole to the surface. This picture of the solvent orientation at the pzc is in essential agreement with similar studies done on mercury.[6]

An analysis of the temperature affect led them to propose that on increasing negative charge of the surface the water dipoles become gradually oriented with the positive pole to the AgI surface. This tendency is then presumably accompanied by an increased structuring in the solvent layer because of the calculated decrease in the surface entropy. On surfaces more positively charged than the surface at which maximum adsorption of alcohols is detected ($-1 \mu C\ cm^{-2}$) the water dipoles are assumed to become oriented the other way around. Based on the calculated increase in surface entropy of such surfaces they conclude that the solvent layer becomes increasingly disordered. This disorder they suggest to be related to the structure breaking effect of the adsorbed counter-ions (anions). This picture of increasing structural disorder when proceeding from a negatively charged surface to a positively charge surface was deduced from studies in the temperature range, room temperature to about 80°C. An analysis of more recently obtained temperature data[7] in the temperature range, 20°–0°C, indicated the change in surface entropy with sign of surface charge to be the inverse from that deduced at higher temperatures. This would suggest a reverse in the ordering of the solvent structure with surface polarization. Apparently the interpretation of the data is not as simple as first anticipated.

This may also be related to the experimental accuracy with which the effects can be measured and to some differences in the composition of the electrolye solution.

Although no definitive picture of solvent structuring near the colloid surface emerges from these studies a new approach to this problem is suggested. The water molecules near the colloid surface find themselves under the reinforcing or the opposing influence of electric fields arising at the solid surface and locally at ions that have penetrated the inner region of the double layer. If structural changes are induced in the solvent these will depend on the degree of hydration and orientation imposed by both the solid surface and by the counter ions. This picture suggests that it might be profitable to treat the solid as if it were a macro-ion and to consider its interaction with the simple counterions across an intervening solvent layer. With this approach one emphasizes the perturbing effect of a macroscopic surface on ion–ion interactions in electrolyte solutions. Structuring or the absence there of in the solvent layer separating the interacting ions will depend on the *type* of p.d. ion adsorbed at the macro-ion and on the counter-ion. A strong interaction between the ions would indicate specific adsorption of the counter ion in the double layer. The effect of the interaction on the solvent structure will depend on the structure-breaking or structure-promoting characteristics of the ions.

This structure promoting or breaking tendency is to be related to the Gurney–Frank model[8,9] of ion–ion interaction in electrolyte solutions.

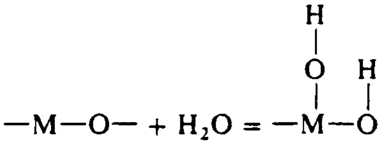
THE DOUBLE LAYER ON OXIDES

Silver iodide is perhaps not the most desirable solid to experiment with if one desires information on water structuring at a colloid surface. There is no reason to expect a strong interaction between this solvent and the uncharged AgI surface. Adsorption studies of water vapor on AgI support this contention.[10] More likely candidates for such an investigation are solid oxides especially the transition-metal oxides. Water plays an active role in establishment of chemical equilibrium between the surface of an oxide and an aqueous solution. The dissociative chemisorption of water on clean oxide surfaces is a well-documented fact.

The heterogeneous reaction through which equilibrium is established between an oxide and the aqueous solution phase may be conveniently represented by the relation:

$$O^{=}(\text{solid}) + H_2O = 2OH^{-}(\text{aq}) \tag{5}$$

This reaction also suggests a potential determining role for both OH^- and H^+ ions at the oxide solution interface. Extensive studies of the electrokinetic behaviour of solid oxides in contact with aqueous solutions of a large variety of uni-univalent electrolytes (including acids and bases) also hint at the p.d. role of these two ionic species[11]. The role of H^+ and OH^- in the formation of the double layer on oxides may be pictured in the following way. Through dissociative chemisorption of water the base oxide surface is covered by anoriented layer of hydroxyl groups firmly anchored to the lattice ions. This initial step may be represented by the hydroxylation reaction:



$$\text{—M—O—} + H_2O = \text{—}\overset{\overset{\displaystyle H}{|}}{\overset{O}{\underset{\;}{\overset{|}{M}}}}\text{—}\overset{\overset{\displaystyle H}{|}}{O} \qquad (6)$$

where M represents the metallic surface cation. The charging of the double layer is conceived as a protonation or deprotonation of the neutral surface sites (OH groups)

$$\text{—M—OH} + H^+ \longrightarrow \text{—M—}OH_2^+ \qquad (7)$$

and

$$\text{—M—OH} \longrightarrow \text{—M—}O^- + H^+ \qquad (8)$$

As one cannot distinguish by conventional means between dissociation of protons from the surface or the adsorption of OH^- ions from solution, the deprotonation reaction[8] may also be written as follows

$$\text{—M—OH} + OH^- \longrightarrow \text{—M—}(OH)_2^- \qquad (9)$$

The surface charge may thus be expressed by a relation similar to that (Eq. (3)) introduced for silver iodide

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}) \qquad (10)$$

Since H^+ is not a constituent of the solid phase its desorption or adsorption from the postulated hydroxylated oxide surface would change its concentration in the surface. The chemical potential of both H^+ and OH^- in the surface will therefore depend on the pH of the solution phase. This means, by analogy to Eq. (1), that the appropriate expression to be used for ψ_0 is

$$\psi_0 = (\mu_H^{s0} - \mu_H^s) + \frac{2.303RT}{F}(pH^0 - pH) \qquad (11)$$

In contrast to the silver iodide system, the simple Nernst equation is not directly applicable to oxide systems. Levine and Smith[12] attempted to find a workable expression for the difference in the surface chemical potential of the p.d. ion by introduction of a statistical mechanical surface model. Their treatment however yielded a relation involving parameters which are not readily accesible to experimental measurement. It should be noted that no major objection can be raised to the application of the Nernst equation in the form

$$\psi_0 = \frac{2.303RT}{F}(\mathrm{pH}^0 - \mathrm{pH}) \qquad (12)$$

to metal hydroxides and oxyhydroxides (e.g. FeOOH).

One would expect the presence of the surface hydroxyl groups, formed by dissociative chemisorption of water, to exert some influence on the water molecules near the surface. In this respect again the oxide surface should be more effective in inducing structuring of water than a silver iodide surface. From an analysis of adsorption, infrared, dielectric and heat of inmersion studies of the Fe_2O_3/water vapor interface McCafferty and Zettlemoyer[13] concluded that one might expect a propagation of hydrogen bonding, stronger than that in the liquid phase, to at least 3 water layers from the oxide surface. This picture of an ordered, immobilised region of physisorbed water on top of the surface hydroxyls would also be applicable to the oxide/liquid water interface.

The metallic lattice ions even though buried underneath the hydroxylated surface would also contribute to the order in the solvent layer .This influence would be exerted through the crystal-field and might be expected to vary from one oxide to another. Attempts have also been made to find a relation between the crystal field electrostatic effect and the observed spread in the pzc values for various oxides[14]. At oxide surfaces two effects, one due to the surface charge and another due to the neutral OH groups, may thus contribute to the ordering of the solvent adjacent to the surface.

Double layer studies on oxides were initiated Bolt[15] and by Parks and de Bruyn.[16] These investigators elected to use the potentiometric titration method which proved so successful in silver iodide adsorption studies. Bolt performed potentiometric acid-base titrations on silica and Parks and de Bruyn on α-Fe_2O_3 (hematite) suspensions. The investigation of α hematite begun by Parks was continued at the Massachusetts Institute of Technology.[17,18] De Bruyn and associates[19,20] also extended their experimental approach to the study of rutile (TiO_2) and the more soluble zincite (ZnO) systems. Other investigators[21–25] also contributed to the experimental double layer studies on oxides. The most detailed and carefully executed study of the double layer on Fe_2O_3 is reported in the recently completed doctoral dissertation by Breeuwsma.[26] Parts of this thesis have already been published elsewhere.[27]

The accumulated adsorption data point to some conspicuous differences between the double layer on oxide materials and on silver iodide or mercury. These differences, we believe, are related to the more active role of water in the formation of the double layer on oxides compare to its "spectator" role in the other two systems. Thus it is found that σ_0 on negative oxide surfaces are much higher for the oxides (~ tens of μC cm^{-2} on α hematite[26]) than for mercury and silver iodide (a few microcoulombs per cm^2). The shape of the adsorption curves ($\sigma_0 - \psi_0$) for Hg and AgI are slightly concave towards the potential axis whereas the adsorption curves on oxides are highly convex towards the pH axis, indicating a steady increase in the adsorption of OH^- with increasing pH. In all three experimental systems the adsorption curves on positive surfaces are convex to the potential axis but the order of magnitude of σ_0 on oxides again exceeds that on AgI and Hg. For most oxide systems the order in the specificity of adsorption of ions belonging to a lyotropic series is the reverse of that found on either mercury or silver iodide. Thus, for example, the specificity in the adsorption of the alkali-metal ions on Fe_2O_3 and on TiO_2 in moderate salt concentrations increase in the order $Li^+ > Na^+ > K^+ > Cs^+$ which is also the order of increasing hydration of the ions. The opposite order in specificity has been observed by Lyklema[2] in silver iodide. Similarly the observed specificity in the adsorption of the halide ions on Fe_2O_3 (as deduced from stability studies by Dumont and Watillon[28]), TiO_2[19] and ZnO[20] is the reverse of that found on mercury. Table I summarizes all available information on the specificity of ion adsorption on oxides. It is significant to note that the order of the adsorption specificity of alkali ions is the same for silver iodide and those oxides characterized by a pH^0 value in the low pH (pH3 and less) range.

There is general agreement among the various investigators that the high "surface" charge can only be accounted for by a spatial distribution of the adsorbed p.d. ions. To avoid the build-up of large electrostatic potentials a partial penetration of counter ions into this volume region is also postulated. As to location and the chemical nature of this region differences of opinion exist. Onoda and de Bruyn[17] proposed that adsorption on hematite is controlled by a superficial shell of hydrated oxide, perhaps similar in composition to goethite. Bérubé, Onoda and de Bruyn[29] studied the diffusion of tritium for hematite (initially contacted with tritiated water) into a non-tritiated water solution. They concluded from an analysis of the kinetic data that the hematite particles were covered by a surface layer which, if goethite-like in composition, would be approximately 13.3 Å thick. Dumont and Watillon[28] made an extensive study of the stability of hematite suspensions as first introduced by Parks and de Bruyn.[16] From measurements of the loss of water on heating their oxide samples they estimated a thickness of 17 Å for a surface hydrated layer with the approximate composition

TABLE I

Oxide	pzc(pH^0)	Adsorption sequence	Investigators
ZnO	9.5–8.5	$Cl^- > Br^- > I^- > ClO_4^- > NO_3^-$	Blok and de Bruyn
Fe_2O_3	8.5	$Li^+ > K^+ > Cs^+$ ($C_{salt} \simeq 10^{-2}N$)	Breeuwsma
		$Li^+ \gg K^+ > Cs^+$ ($C_{salt} > 10^{-}N$)	Breeuwsma
	6.5	$Mg^{2+} \gg Ca^{2+} > Sr^{2+} > Ba^{2+}$ ($C_{salt} > 10^{-2}N$)	Breeuwsma
	8.5	$F^- > Br^- > NO_3^- > Cl^- > ClO_4^- \simeq I^-$	Dumont and Watillon
β-MnO_2	7.3	$Li^+ > Cs^+$	Stumm, Huang and Jenkins
Cr_2O_3	7	$Li^+ > Cs^+$	Weiser[a]
TiO_2	6	$Li^+ > Na^+ > Cs^+$	Bérubé and de Bruyn
		$Cl^- \geq ClO_4^- > NO_3^- > I^-$	Bérubé and de Bruyn
SiO_2 (quartz)	3.7	$Cs^+ \geq Li^+$	Malati[b]
SiO_2	2.3	$Cs^+ > Li^+$	Jadros and Lyklema
δ-MnO	1.5	$Cs^+ > Li^+$	Stumm, Huang and Jenkins
WO_3	0.5	$Cs^+ > Li^+$	Weiser[a]

[a] H. B. Weiser, Inorganic Colloid Chemistry (Wiley, N.Y., 1935), Vol. 2, 140, 317.
[b] M. A. Malati, *Disc. Faraday Soc.*, No. 52, 377 (1971).

$Fe_2O_3 \cdot 2.8H_2O$). It might be argued that the thin surface layer of different composition from the core material in these experiments may be due to incomplete crystallizations of the product formed during hydrolysis. Breeuwsma[26] prepared α-Fe_2O_3 by a different technique which involved the addition of an equivalent amount of base (KOH) to a boiling solution of ferric nitrate, followed by a treatment in an autoclave to promote complete crystallization. From differential thermogravimetric analyses and on assuming the surface of his samples to have a goethite-like composition, he estimated this surface layer to have a thickness varying between 15 and 25 Å. This calculated thickness represents about 10% of the equivalent particle radius. Breeuwsma's results support the existence of a disturbed surface on hematite and which is not due to incomplete crystallization of the precipitate.

These studies of the surface composition of hematite suggests that the hydroxylation of the surface is not confined to a layer one molecule thick. They support the spatial distribution model for explaining the high surface charge and also suggest that the Nerst relation (Eq. (12)) might be used with some justification to calculate ψ_0. At least, one might conclude that the dependence of μ_H^s on solution pH may not be as marked as originally anticipated.

Lyklema[30] developed a mathematical model to describe in a quantitative way the penetration of ions into the solid. His model provides no insight in the physical and chemical nature of this volume region. It simply assumes an exponential decrease of σ_0 with increasing distance from the oxide surface and a Langmuir-type expression to account for the adsorption of the counterions that penetrate the solid. He was able to show that it is possible with this model to reproduce the characteristic shape of the adsorption curves. By choosing appropriate values for the adjustable parameters-penetration depth, dielectric constant, and specific adsorption potential—which appear in the Lyklema treatment, Breeuwsma was able to reproduce the experimental (σ_0-pH) curve for hematite in IN LiCl solutions.

Tritium exchange studies on TiO_2[19] do not support the existence of a three dimensional hydroxylated surface layer on this oxide. To explain the high surface charge on rutile Berube and de Bruyn[19] proposed that the region accessible to penetration by the p.d. ions and partly by counterions must be located on the solution side of the oxide surface. They visualized a structural layer of "frozen" water to be formed. The rutile particle is treated as a macroion which because of the structure-promoting nature of both the OH^- and H^+ ions not only polarizes and immobilizes water molecules in the first layer adjacent to the oxide surface but induces additional order beyond the first layer. Since small cations such as the Li^+ ion tend to produce the same effect on the solvent (because of their high electrostatic fields) they are able to penetrate the structured water region and are therefore more strongly adsorbed than the bulkier ions.

A similar interpretation were given by Dumont and Watillon to explain the observed coagulation sequences on hematite. They suggest that at low values of ψ_0 (or of the difference, pH–pH^0), the structured water layer at the interface maintains all ions sufficiently far away from the surface but on increasing ψ_0, the electrostatic attraction becomes high enough to pull the ions into the layer where they are specifically adsorbed. With increasing ψ_0, the proposed specificity in ionic adsorption would be strong structure promoters > low structure promoters > low structure breakers > strong structure breakers. The reversed sequence would occur if the colloidal ion has a disordering effect on the solvent layer. Lyklema and Breeuwsma[26,27] agree that the observed specificity of alkali metal ions on hematite in moderate salt concentrations is probably best explained by a model based on ion-ion interactions of the Gurney-type. They are, however, inclined to explain the observed specificity at higher salt concentrations ($> 10^{-2}N$)

$$Li^+ \gg K^+ \simeq Cs^+$$

by an exchange between Li^+ and lattice Fe^{+++} ions. They point out that the crystal ionic radii of these elements are almost equal and therefore it should be possible for the Li^+ cation to occupy the octahedral Fe^{3+} sites in the crystal lattice. It is known that Li^+ and Fe^{3+} are randomly distributed over octahedral sites in the ferrite compound $LiFeO_2$ which has the NaCl crystal structure.[30] The exceptional behaviour of Mg^{++} in the specificity of the alkaline-earth metal sequence on hematite is also explained by this penetration and exchange model.

According to the Berube–de Bruyn model of the oxide interface the "normal" specificity of alkali metal ions observed on silica, δ-MnO_2 and WO_3 suggests that these surfaces behave as structure breakers. Stumm, Huang and Jenkins[31] suggest that this inversion in the specificity of the alkali metal ions may be largely accounted for by the influence which the electrostatic field strength has on the structure of the adjacent water layers. The higher this effect the greater the structure promoting ability of the oxide surface. As a measure of the crystal field strength for different oxides they calculate the volume of the unit cell per central ion which should be inversely proportional to this effect. Such calculations yield the following results: AgI (54 Å^3), δ-MnO_2 (44 Å^3), Fe_2O_3 (25 Å^3), β-MnO_2 (27.6 Å^3), TiO_2 (26.2 Å^3) which are in agreement with the specificity measurements.

Whether this picture of ionic interactions at oxide surfaces may be applied without modification to the oxide, silica, is debatable. Kitchener[32] has pointed out that when silica is precipitated from aqueous solution it is incapable of condensing into a compact crystalline form. Its outer surface would probably consist of extended chains of polysilicic acid which would exert an important influence on the adsorption characteristics of this oxide and its stability behaviour. The exceptionally high surface charges measured by Tadros and Lyklema[22] on precipitated silica and the anomalous stability of this oxide at the pzc underscore the remarks of Kitchener.

This review of the properties of colloid surfaces may be concluded by the following general observation. Structuring of water at oxide surfaces is implied by experimental measurements of the adsorption of p.d. ions and foreign ions and stability of oxides uspensions. It is however, obvious that a quantitative picture of conditions at the oxide-aqueous solution interface will require the development of novel experimental techniques and the introduction of statistical models of the interphase.

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Discussion of the Report of P. De Bruyn

Depasse. A number of phenomena, in colloid chemistry, could be clarified by keeping the ideas of Desnoyers about the structural interactions between solutes in water.

1 *The high stability of silica at the zero point of charge and the Hofmeister sequence of cations on its surface.* The silica surface is strongly hydrophilic

and is covered with silanol groups which orient water in the same direction as small cations, such as Li^+, do. Thus we must observe an increasing repulsion between the silica surface and the cations, when the hydrophobicity of the cations increases (hydrophilic repulsion, same sign, in the theory of Desnoyers). Indeed, we have in order of increasing adsorption of monovalent cations on silica:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < \text{Choline} < TMA^+ < TEA^+$$

On the other hand, the stability of silica sols at the zero point of charge can also be explained by the existence of a repulsion force between two hydrophilic particles which orient water in the same direction, the protons of water pointing outwards.

2 *The behaviour of* Fe_2O_3 *and* TiO_2 *sols.* For Fe_2O_3 and TiO_2, reversed Hofmeister series of adsorption of ions have been observed. Berube and de Bruyn for TiO_2[1] and Dumont and Watillon for Fe_2O_3[2] have explained the inversion of the sequence by the localized hydrolysis process, or by a mechanism of attraction between a structure-making surface and structure-making ions. Desnoyers has classified such mechanisms as "hydrophilic-hydrophilic (opposite sign) attractions." The repulsion mechanism plays the leading part for silica and the attraction mechanism does it for Fe_2O_3 and TiO_2, because the silica surface is essentially acidic, and orients water in one direction and can orient water in both directions. On amphoteric surfaces, small hydrophilic ions can always find a great number of water molecules which are oriented in such a direction that they can form "hydrophilic-hydrophilic bondings" with them. Similarly, the fact that hematite and rutile are unstable at their zero point of charge can be explained by the formation of hydrophilic-hydrophilic interparticle bonds.

3 *Interactions between hydrophobic particles and ions, and between hydrophobic particles themselves.* Polystyrene particles have more hydrophobic surfaces than oxyde particles, and we can predict the Hofmeister series of adsorption of ions (hydrophobic bonds between surface and ions) and interparticle hydrophobic bonding). Indeed, we have observed that a polystyrene sol was better coagulated by TMA^+ than by Na^+, and it is well known that those sols are very unstable at their zero point of charge.

It seems that the same hypothesis could explain the behavior of electrolyte solutions and of colloidal sols, even without resorting to the concept of long range Van Der Waals forces between colloidal particles.

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De Bruyn. Does your model for quartz apply in all respects to other oxides with a pzc below 3? For example, WO_3 and some form of MnO_2?

Depasse. I suppose, but those surfaces are not very well known.

Desnoyers. If structural attraction and repulsive forces really exist in aqueous electrolyte solutions, as I think they do, then they must also exist near colloidal particles and electrodes. The experiments and interpretation of Dr. Depasse seem most interesting.

Watillon. On one hand, calculating the Van der Waals attraction between two silica spheres embedded in water, due to the very low constant of silica, we got a Hamaker constant which was an order of magnitude smaller than the value generally encountered for colloids. This fact explains why an adsorbed layer could already be sufficient to prevent coagulation and why this colloid does not follow the D.L.V.O. theory and has for instance its maximum of stability at its point of zero charge.

On the other hand, Hamaker constants of Fe_2O_3 and TiO_2 are important, and long range Van der Waals forces cannot be neglected for these oxides, although they have superficial hydration layers. Nevertheless, the very weak heat of immersion of silica (~ 100 ergs/cm^2) would tend to assign this surface to the class of the more hydrophobic ones (in comp. with Fe_2O_3 and TiO_2 ~ 500–600 ergs/cm^2). To try to understand this fact, we would like to mention a recent communication of Dr. Kitchener[1] who stressed the importance of polysilisic acid residues on the surface, which hinder the particle approach. Cleaning the surface by leaching in alkaline medium transforms the system in a D.L.V.O. colloid, coagulating at the point of zero charge.

In our laboratory, Mr. D. Germain[2] prepared spherical amorphous SiO_2 particles according to the Stober[3] method and studied the kinetics of coagulation of these sols after leaching. He observed a linear decrease of the stability with decreasing pH, and a minimum value at the point of zero charge, irrespective of the nature of the ion.

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Parsons. It seems to me that there is very good experimental evidence for the existence of the discreteness of charge effect, for example the Esin and Markov effect and the directly related dq^1/dq. However, it is not at present possible to distinguish experimentally between the sophisticated developments of this effect due to Levin *et al.*,[1] MacDonald and Barlow,[2] and Levich *et al.*[3]

De Bruyn. Expresses his full agreement with Dr. Parsons.

Randles. I would like to ask Professor de Bruyn if he can explain the results of a simple little experiment carried out a few weeks ago by one of my students. A small bubble of air or nitrogen was released from a fine capillary tube a few mm below the free surface of an electrolyte solution in a glass tube. The surface formed a convex meniscus and the small bubble rested in the centre of this. The time between the bubble reaching the surface and bursting (i.e. coalescing with the air phase) was measured. The lifetime of the bubble was fairly reproducible and an average for about 100 bubbles was taken. For NaCl solutions it varied with concentration according to a curve presenting a maximum.

Parsons. I wonder whether Randles' experiments could not be explained by a combination of the effect of slow draining increasing by the electroviscous effect (cf. soap water draining), followed by the reduction in repulsion at very high ionic strength.

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Randles. I agree with Dr. Parsons that the maximum may be due to the opposing effects of a kinetic (liquid drainage) factor and a diffuse layer repulsion.

Watillon. The properties of oxide/water interface have generally been deduced from adsorption isotherm determinations. Our investigation represents an attempt to study the same problem by another approach, viz. the kinetics of coagulation.

We studied ferric oxide hydrosols in the presence of various monovalent ions in the pH-range 2–12.5; the point of zero charge is situated at pH 8.2. As an example, we present on Figure V.1 the concentrations of coagulation against pH for positively charged ferric oxide and a series of monovalent anions. The common slope (about ~45°) represents either partial, or total behaviour of all the ions when they behave in an aspecific manner; this line

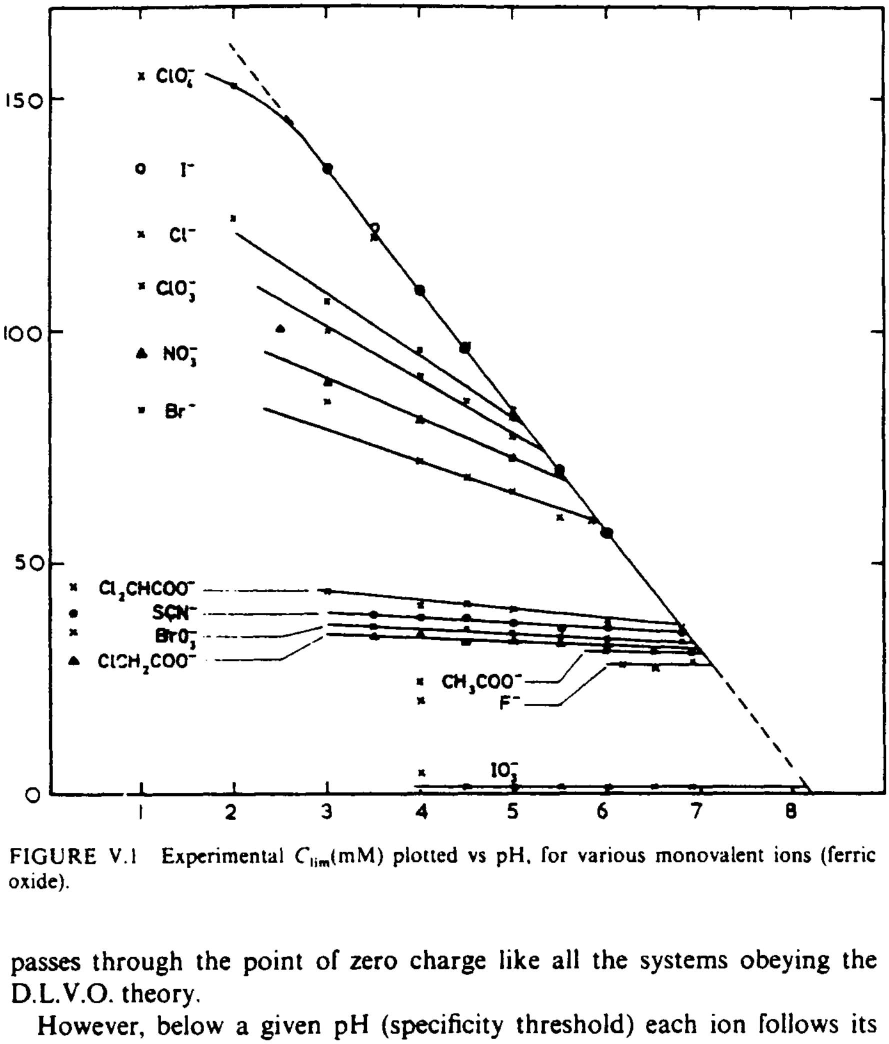

FIGURE V.1 Experimental $C_{\lim}$(mM) plotted vs pH, for various monovalent ions (ferric oxide).

passes through the point of zero charge like all the systems obeying the D.L.V.O. theory.

However, below a given pH (specificity threshold) each ion follows its own way and becomes specifically adsorbed.

At extreme pH values, the following adsorption sequences have been found. In acidic media, $IO_3^- > F^- > CH_3COO^- > CH_2ClCOO^- > BrO_3^- > SCN^- > CHCl_2COO^- > Br^- > NO_3^- > ClO_3^- > Cl^- > ClO_4^- \sim I^-$, and in alkaline media $Li^+ > Na^+ > K^+ \sim Cs^+$.

The general trend is thus clearly indicated; the most structure-promoting ions are the most strongly adsorbed, while the typical structure breakers are not. On the one hand, ClO_4^- seems, on the higher pH scale, to be non-specifically absorbed; on the other IO_3^-, although relatively large in size, has so weak $I = O$ bindings that oxygen atoms can exchange very rapidly with those of water. IO_3^- behaves thus like a small ion, with its structuring properties explaining the large specific adsorption observed.

The drastic difference between ClO_4^- and IO_3^- at pH 3 is shown by their coagulation values: $C_{ClO_4^-} = 135$ mM and $C_{IO_3^-} = 2$ mM. It is thus clearly shown that the ferric oxide behaves, in the Gurney theory, as a macroion with structure—promoting surface properties. We compared the observed adsorption sequence on ferric oxide with those measured on weak acid[1,2,3] and weak base[4] ion-exchange resins, which behave as structure promoting surfaces, and also to activity coefficients of the corresponding acids and bases[5] and to the B coefficients of viscosity[6] which reflect ion–ion and ion–solvent properties. Analogous series have previously been obtained in electrode kinetics by Gierst *et al.*[7]

It seems interesting to point out that these attempts to use Gurney theory and their recent improvements allow to generalize the interpretation of parallel phenomena in the field of electrochemistry, surface chemistry and colloid chemistry.

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Parsons. I am surprised that F^- is so strongly adsorbed on Fe_2O_3. Is there some other evidence for strong interaction between F^- and Fe_2O_3? Apart from this ion the order of adsorption seems similar to that on Hg.

Ubbelohde. Interesting examples have been quoted in the report by Professor de Bruyn and in the discussion, concerning effects of e.g. proton attachment to solid oxide surfaces, on the aqueous ionic layers in contact with them.

What seems less apparent is the role of dispersive attractive forces of atoms in the solid, for water molecules in the layers immediately adjacent. One might expect, for example, that solids with atoms of high atomic number example, that solids with atoms of high atomic number with many electrons, such as tungsten or uranium, could (when clean) attract H_2O molecules relatively much more strongly than, say, solides such as beryllium or aluminium. Is this a false expectation, or is the effect masked by other more powerful forces?

Parsons. The dispersion forces are taken account of in the calculation of the Hamaker constant.

De Bruyn. Compared to the electrostatic contribution, that of the dispersion effect is quite small. The estimated Hamaker constants for a large number of materials including some metallic sols lie between 10^{-13} and 10^{-12} ergs.

Watillon. In order to describe the attraction-distance relationship between two approaching colloidal particles, historically, the starting point was the equations for atoms or molecules like those of London,[1] Slater-Kirkwood,[2] Hellman,[3] Moelwijn-Hugues[4] and Neugebauer.[5] By successive integrations, Hamaker deduced relations for colloids (microscopic relations) which can unfortunately not be used for metals because knowledge of the polarizability is needed.

More recently, relations have been derived from the classical Landau and Lifshitz theory and adapted to colloids[6]; they represent a macroscopic approach of the problem, in which the dispersion forces are calculated from the integral of the imaginary part of the refractive index on the electromagnetic spectrum; this method can be applied for dielectrics and for metals.

For dielectrics, like colloidal suspensions of polystyrene in water, experimental determinations of Hamaker constant fit the microscopic and the macroscopic approaches.

For metals, especially of high atomic number, the macroscopic theory gives Hamaker constants one order of magnitude larger than the value obtained experimentally from colloids. The theoretical value is incompatible with the existence of a colloidal state for these metals. This indicates that the model has to be improved and that a colloidal metal particle is probably surrounded by an adsorbed layer presenting a much lower Van der Waals constant than the metal itself (much closer to the value of the dispersion medium), and weakening the interparticle attraction forces by a shell effect.

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Behr. Professor de Bruyn has mentioned in his lecture the unusually strong adsorption of F^- ions on the iron oxide surface, a behaviour much different from that of the F^- ions at a mercury surface. It may be perhaps explained by a sort of chemical bonding at the solid surface, as F^- do form stable complexes with Fe^{+++} and not with mercury. At the mercury surface the species containing sulphur with non-bounded electron pairs seem to exhibit relatively strong adsorption effects which could be related to the great chemical affinity of sulphur and mercury. The same is true of anions which form stable mercuric complexes, like I^- or SCN^-.

Magat. I have the impression that the problem treated by Professor de Bruyn is extremely complicated and, I fear, insoluble by a direct attack.

I don't know these questions at all, but I am wondering if it would not be a good strategy to disentangle first the problem of colloidal solutions or suspensions in non polar media, and then in water, but avoiding ionic or metallic particles particularly difficult to treat (eventually suspensions with soap layers, whose structure is more or less understood, and to treat only *afterwards* the most complex cases).

Parsons. This approach has been used by Kitchener[1] using polystyrene particles with sulphonate groups, by Ottewill[2] using latices and by Pethica[3] using oil (octodecanol) on which surfactants were adsorbed. Although the latter in particular seems a logical way to approach the problem, these results did not seem to lead to a great clarification.

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