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HIGH FREQUENCY TRANSPORT PROPERTIES OF  
COLLOIDAL DISPERSIONS

ROBERT J. HUNTER



The Royal Society of New South Wales



**Robert John Hunter**

### ROBERT JOHN HUNTER 1933 -

**Robert John Hunter** was born on 26 June, 1933 at Abermain, NSW. He was educated at Abermain Public School (1938-1944) and then at Cessnock High School (1945-1949), while holding State Bursaries. With a Public Exhibition and University Bursary he entered the New England University College (then a College of the University of Sydney) in 1950 and shared the Prize for the best First Year Pass. He graduated B.Sc. in 1954, in the meantime having been Master of Maths and Science at Wolaroi College for Boys, Orange, NSW for the period July 1953 - June 1954. He was then appointed as Technical Officer and subsequently became Experimental Officer as a chemist in the Division of Plant Industry, CSIRO, Deniliquin, NSW. In 1957 he went to the University of Sydney as a Ph.D. student with a Graduate Scholarship from the CSIRO Division of Soils; he worked with Professor A.E. (Alex) Alexander on the flow of colloidal suspensions through porous media, and graduated Ph.D. in 1962. In mid-1960 he was appointed Experimental Officer, Division of Soils, CSIRO, Canberra, and in late 1961 was promoted to Research Officer in that Institution. In 1964 he was appointed as Lecturer in Physical Chemistry at the University of Sydney, where he was promoted to Senior Lecturer in 1967, and Associate professor in 1972. For the period 1987-1990 he was Head of the School of Chemistry, then he formally retired, becoming an Honorary Associate Professor. During periods of study leave he was Visiting Senior Lecturer, University of Queensland (1968); and Visiting Professor at James Cook University of North Queensland, Townsville (1971-72); University of Bristol (U.K.) (1974); University of California at Berkeley (1979); University of Canterbury, Christchurch, New Zealand (1982-1983); and Ecole Polytechnique de Lausanne, Switzerland (1986). At most of these institutions he gave courses on colloid science at either the graduate or undergraduate level. In 1998, he was Visiting Professor at the University of Göteborg, Sweden where he gave a graduate course in colloid science.

Bob Hunter served on numerous boards and committees at the University of Sydney between 1964-1999 and was Sub-Dean, Faculty of Science, (1970-1971) and Pro-Dean (1978-1979). He was on the Editorial Board of the *Journal of Colloid and Interface Science* (1980-1982) and of *Colloids and Surfaces* (1980-1983), becoming Editor for the latter journal (for Asia and Australia) during 1984-1990. He was President of the International Association of Colloid and Interface Scientists for the period 1992-1994.

#### Honours and Awards (pre-2014)

1975	FRACI
1982	Archibald D. Ollé Prize, RACI
1986	FAA
1987	A.E. Alexander Memorial Lecture, RACI
1988	Liversidge Research Lecture, Royal Society of New South Wales
1994	Archibald D. Ollé Prize, RACI

## **Biographical Source**

Personal Communication

### **Scientific Publications by R.J. Hunter**

Between 1960 and 1997 R.J. Hunter published some 81 papers, 11 reviews, 4 book chapters, and 8 books - mainly on colloid chemistry.

## HIGH FREQUENCY TRANSPORT PROPERTIES OF COLLOIDAL DISPERSIONS\*

ROBERT J. HUNTER

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**ABSTRACT** Colloidal dispersions occur in a wide range of scientific and technological situations and their proper characterisation is an important area of scientific activity. Almost all colloidal systems are composed of particles which carry a net electrical charge on their surfaces, unless special precautions are taken to remove that charge. Indeed, apart from particle size and shape, electrical charge is probably the most important property determining the behaviour in almost all situations.

Both the static (equilibrium) and the kinetic charge are normally determined and the two values used to develop a picture of the charge distribution in the region around each particle. That information can then be used to calculate the electrostatic interactions between the particles and hence, to estimate many important aspects of behaviour.

This paper describes some important new techniques for estimating the magnitude of the charge and its distribution in the neighbourhood of the surface. Important new insights are gained from the study of the conductance and dielectric behaviour at high frequencies (around 1 MHz) and by the study of the interaction of ultrasonic waves and electrical fields at the same frequencies.

### Introduction

The work I will describe is based on the theoretical analysis of my colleague, Dr Richard O'Brien. His reexamination of the current theory of high frequency conductivity of colloidal sols and the behaviour of ultrasonic waves in colloidal suspensions has enabled us to focus our experimental activities to maximum effect. The experimental studies have been undertaken by Dr Brian Midmore with the assistance of two Honours B.Sc. students: David Diggins and Andrew Shortland. All have contributed to the material I shall describe.

### Determination of the Fixed Charge on a Colloid

For certain colloidal systems, such as the mineral oxides and classical sols like silver iodide, the surface charge can be attributed to the adsorption of particular inorganic ions on the surface. Thus, for oxides it is the hydrogen or hydroxide ion which determines the charge and that charge varies from positive to negative as the pH is increased in much the same way as for a protein. These ions are called the *potential determining ions (p.d.i.)* and the number adsorbed can be estimated by titrating the

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colloidal sample with acid or base. By comparing the amount of reagent necessary to induce a certain change in pH of the suspension with the amount required to induce the same change for the background electrolyte, one can estimate the number of  $H^+$  or  $OH^-$  ions adsorbed and, hence, the surface charge,  $\int_0$ . The only additional parameter required is the pH at which the sample has no charge (the *point of zero charge* or *p.z.c.*).

The charge on the colloidal particle is balanced by an equal and opposite charge in the surrounding solution and the combination is referred to as the *electrical double layer*. This charge distribution is governed by a balance between the electrostatic forces which draw the ions towards the surface and the thermal diffusive forces which tend to spread the charge away from the surface. Some of the countercharge may be stuck closely to the surface in the compact region whilst the remainder appears as a *diffuse layer* around the particles. (Fig.1).

### Determination of Kinetic Charge

The kinetic charge is determined by observing the velocity of the particles in an electrical field. It is usually smaller in absolute magnitude than the surface charge because some of the counter charge remains firmly attached to the particle and moves with it in an electric field. The kinetic charge is an important parameter nonetheless because it seems to give a good estimate of the charge in the diffuse part of the double layer (Fig. 1). This represents the charge which is 'seen' by another approaching particle more closely than does the total charge and is therefore the more appropriate quantity to use in calculations of interaction energy.

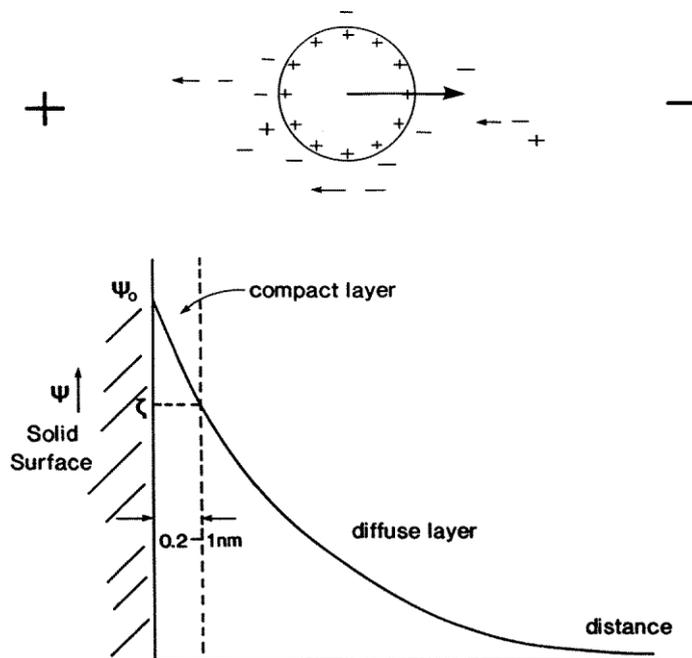


FIGURE 1. The standard model of the Double Layer showing the division between the compact and the diffuse part. In the compact region, the structure is determined by the details of molecular size and dipole / charge interactions as well as specific (chemical) effects. In the diffuse region, the forces are more physical in nature (electrostatic and thermal diffusion).

## Conductivity and Dielectric Behaviour of Colloidal Suspensions

The theoretical description of the effect of an electric field on a colloidal dispersion is best considered under two separate regimes: the low frequency (<10 kHz) and the high frequency (1 - 10 MHz) regions. The dominating physical processes are different in the two cases. It is also appropriate to distinguish the theoretical treatments at low and high concentration since the approximations and limitations are different in the two cases. So too are the experimental difficulties. We have been able to study the high concentration systems at both high and low frequency but our apparatus was not sufficiently sensitive to make accurate measurements on dilute systems at high frequency.

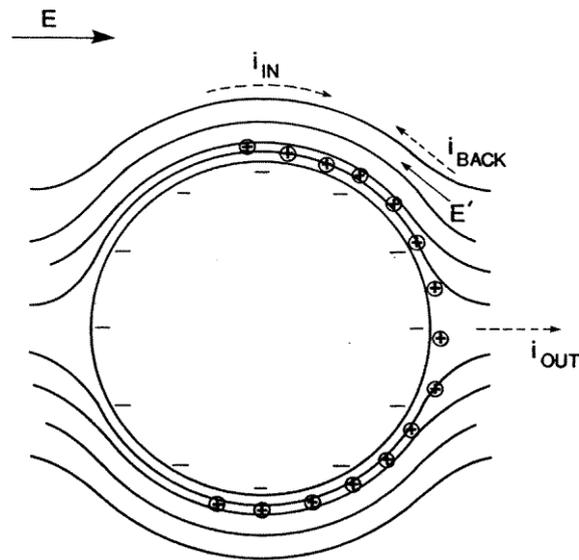
The conductivity is, in general, a complex quantity with real and imaginary parts which depend in different ways on the frequency. These parts measure the dissipative and storage processes which occur when an electric current passes through a colloidal suspension.

What emerges from this theoretical and experimental work is the significance of a parameter which we designate  $\lambda$ : the *surface conduction parameter*. It is defined as:

$$\lambda = K_s/K^\infty a \quad \dots\dots\dots (1)$$

and measures the ratio of the conductivity through the double layer ( $K_s$ ) to the value for the bulk electrolyte ( $K^\infty$ ). The particle radius,  $a$ , enters to make  $\lambda$  dimensionless. The theory allows the experimental results under all conditions (low and high frequency and low and high particle concentration) to be described with this one adjustable parameter and with no assumptions about the detailed structure of the electrical double layer around the particle. The only approximation involved is the assumption that the double layer is thin compared to the radius of the particles ( $\lambda a \gg 1$ , where  $\lambda$  is the Debye-Hückel parameter). In practice this is the normal situation for particles bigger than about 100 nm; for smaller systems, like proteins, it will be true only at higher salt concentrations (> 0.1 M say). Only if one wishes to interpret  $\lambda$  in terms of particle charge is it necessary to introduce a double layer model and, as we shall see, even that is comparatively straightforward.

To understand the behaviour of the sol under the influence of a high frequency electrical field, consider the situation shown in Fig. 2. When the field is applied, the charges on the particle itself are assumed to be fixed but those in the double layer are able to respond. They will move in the direction indicated and are able to do so in a time of order  $10^{-6}$  seconds. It is this relaxation process which dominates at megahertz frequencies. The movement of those charges backwards and forwards as the field direction changes is analogous to the behaviour of a dipole, and indeed, the particle is best characterised by its *dipole strength*,  $S$ , which is a complex quantity. The real and imaginary parts of  $S$  measure the in-phase and the out-of-phase components. In Fig. 3 the experimental data for  $S$  is matched to the theory using a least squares procedure with  $\lambda$  as the adjustable parameter.



$t \sim 10^{-6} \text{ s}$

STEADY STATE REACHED WHEN

$$i_{IN} - i_{BACK} = i_{OUT}$$

FIGURE 2. The polarisation of the double layer under the influence of an applied electric field. This movement takes place in a time of the order of  $10^{-6}$  seconds.

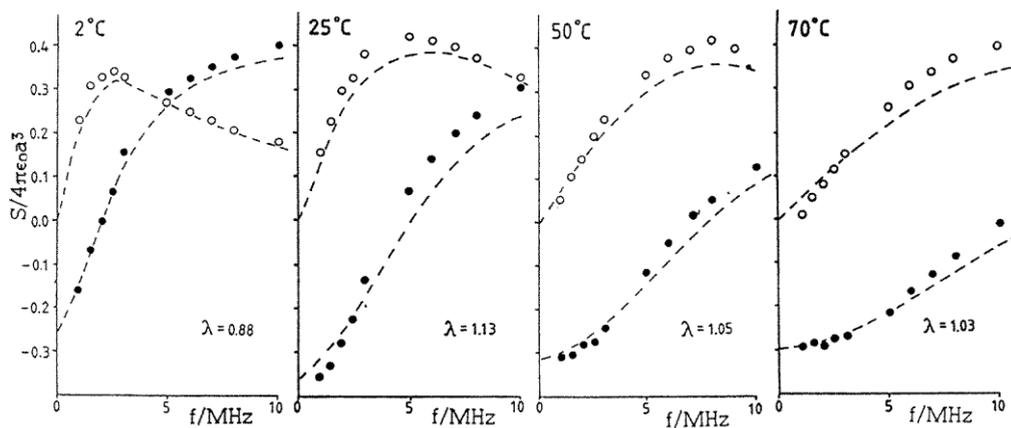


FIGURE 3. The dipole strength (in dimensionless units) as a function of frequency at several temperatures. The values of  $\lambda$  are essentially constant despite a change of three fold in the bulk conductance.  $\circ$  Real and  $\bullet$  Imaginary part of  $S$ .

At low frequencies the dipole can keep pace with the field so the imaginary part is zero (Fig. 3). It rises to a maximum at about the *relaxation frequency* of the double layer ( $\Sigma/K^\infty$ , where  $\Sigma$  is the permittivity) and then would fall to zero again as the

frequency rises to a value where the ions no longer attempt to move. This occurs at about 20 MHz and at frequencies above that value the particles behave as though they were uncharged. The  $\lambda$  values shown in Fig. 3 show relatively little variation, considering the fact that the bulk conductivity shows a change of around 300% over this temperature range.

What sparked our interest in the parameter  $\lambda$  was the fact that when it was interpreted in terms of the standard double layer model, it yielded a value for the diffuse layer charge which was almost identical to that obtained for the total charge by titration,  $Q_0$ . For particles with such a low charge density (about  $3 \mu\text{C cm}^{-2}$ ) it would not be surprising to have the total and the diffuse layer charges equal: the electrostatic forces on the countercharge would not be expected to pull many ions into the compact region. It seemed likely, therefore, that we had here a means of directly measuring the diffuse layer charge and potential, quantities which are only rarely accessible and then only with considerable experimental effort.

### Relation Between $\lambda$ and Double Layer Charge

The simplest double layer model is that in which the shear plane, where the electrokinetic potential,  $\psi$  is measured (Fig.1), corresponds to the beginning of the diffuse part of the double layer. If it is assumed that, outside that plane, the ions and the fluid are able to move in response to the field but inside it, they are fixed to the particle, then it can be shown that:

$$\lambda = \frac{K_S}{K^\infty a} = \frac{\exp(\tilde{\psi}/2)(1 + 3m/z^2)}{\kappa a} \dots\dots\dots (2)$$

where  $\tilde{\psi}$  is the reduced (dimensionless)  $\psi$  potential, equal to unity for  $\psi = 25.7 \text{ mV}$  at  $25^\circ\text{C}$ .

$m$  measures the ionic mobility in the double layer, and  $z$  is the valency of the counterions.

Given the value of  $\psi$ , the diffuse layer charge,  $Q_d$ , follows directly from the standard Gouy-Chapman theory of the diffuse double layer:

$$Q_d = A c^{1/2} \sinh(\tilde{\psi}/2) \dots\dots\dots (3)$$

where  $A$  is a (dimensional) constant and  $c$  is the electrolyte concentration.

A more sophisticated model, and one which we have found useful for the description of the behaviour of latex systems, draws a distinction between the plane of shear and the beginning of the diffuse double layer. In this model (Fig. 4) ions and liquid can move outside the shear plane but, in the region between the beginning of the diffuse layer and the shear plane, only the ions are able to move in response to the field. Inside the compact layer neither the ions nor the liquid can move.

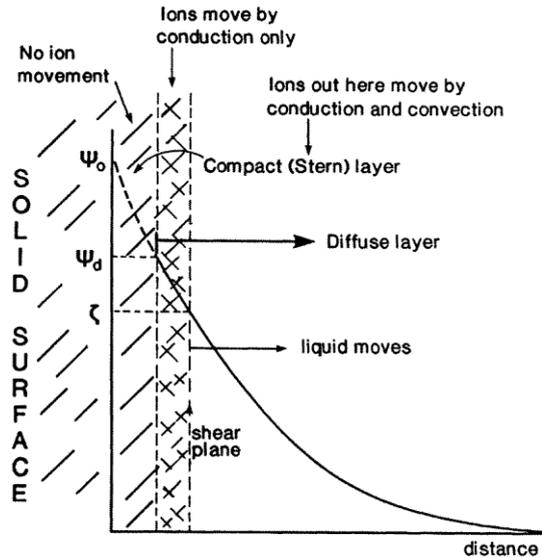


FIGURE 4. A more sophisticated model of the double layer in which some diffuse layer ions are permitted to move under the influence of an electric field without motion of the surrounding liquid.

A similar model had been introduced by Bikerman (1935) and modifications have been used since in various contexts (Dukhin and Deryaguin 1974). Our usage is consistent with at least some of those earlier ones but has the advantage that we are able to combine results from both the conductance and the electrokinetic work and so strengthen the conclusions from the model. According to Bikerman, the surface conduction for the model shown in Fig. 4 is given by:

$$K_S = \left\{ \kappa_d + \frac{2\zeta RT}{z_+} \frac{e l^+}{\eta} \right\} / F \quad \dots\dots\dots (4)$$

where  $F$  is the Faraday constant and  $\eta$  the solvent viscosity. The subscripts  $d^+$  and  $e l^+$  refer to diffuse layer and electrokinetic charge respectively, whilst  $\kappa_+$  is the equivalent conductance of the cation. The first term in the braces is the conductance and the second term measures the ion flow due to convective transport with the electro-osmotic flow of the liquid. Using the experimental value of  $\lambda (= K_S/K^\infty a)$ , the value of  $\kappa_d$  could be estimated if we could estimate  $e l^+$ .

At first sight it would appear that the value of  $e l^+$  would follow immediately from the  $\psi$  potential using equation (3), but that is true only if the correct value of  $\psi$  is used. When the ions behind the shear plane are able to conduct an electric current (called *anomalous conductance*) the usual expressions for  $\psi$  are in error. Even the more sophisticated models of Overbeek (1943), Booth (1950) and O'Brien and White (1978) only allow for conductance outside the shear plane.

Fortunately, it is possible to make the necessary correction. In the presence of anomalous conduction the electrophoretic mobility function  $E_m$  for large  $\lambda a$  is given by (O'Brien 1986):

$$E_m = \frac{3}{2} \left( 1 + \frac{3}{2} \frac{\lambda a}{\kappa_+} \right) \dots\dots\dots (5)$$

where the first term is the Smoluchowski expression. Thus the measured value of  $\zeta$  gives  $K_S$  and also corrects the  $\psi$  potential so that an estimate of  $\psi_d$  can be obtained from  $K_S$ .

TABLE 1  
Effect of Changing 'Indifferent' Co-Ion on  $\psi_d$  and  $\psi_{el}$ .  
The Counterion is  $K^+$  in Each Case.

Ion	$K^\infty$ mS cm <sup>-1</sup>	$\zeta$	$\psi_{el}$ $\mu\text{C cm}^{-2}$	$\psi_d$
Br <sup>-</sup>	1.44	0.140	4.4	6.6
Cl <sup>-</sup>	1.42	0.147	3.9	7.2
NO <sub>3</sub> <sup>-</sup>	1.39	0.149	4.1	7.1
SO <sub>4</sub> <sup>2-</sup>	1.34	0.151	4.7	6.6
F <sup>-</sup>	1.21	0.175	4.1	7.3
IO <sub>3</sub> <sup>-</sup>	1.09	0.206	3.9	7.9
CH <sub>3</sub> COO <sup>-</sup>	1.03	0.201	3.1	7.3
Titration Charge = - 6.7 $\mu\text{C cm}^{-2}$ .			Mean = 7.1	

TABLE 2  
Effect of Changing the Counterion on the Diffuse and Electrokinetic Charges  
for a Latex in 0.01 M Chloride Solution.

Ion	$K^\infty$ mS cm <sup>-1</sup>	$\zeta$	$\psi_{el}$ $\mu\text{C cm}^{-2}$	$\psi_d$
Li <sup>+</sup>	1.06	0.120	3.7	7.0
Na <sup>+</sup>	1.21	0.135	4.3	7.4
K <sup>+</sup>	1.42	0.147	3.9	7.1
NH <sub>4</sub> <sup>+</sup>	1.42	0.156	4.2	7.7
Cs <sup>+</sup>	1.45	0.118	3.8	5.3
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	1.12	0.052	2.6	2.5
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N <sup>+</sup>	1.01	0.018	1.6	0.9

TABLE 3

*Effect of Various Counterions on the Diffuse and Electrokinetic Charge for a Cationic Latex Dispersed in 0.01 M K<sup>+</sup> salts.*

Ion	$\kappa^\infty$ mS cm <sup>-1</sup>	$\lambda$	$\psi_{el}$	$\psi_d$ $\mu\text{C cm}^{-2}$
F <sup>-</sup>	1.21	0.169	-3.1	-8.7
Cl <sup>-</sup>	1.41	0.141	-2.3	-6.8
Br <sup>-</sup>	1.41	0.120	-2.1	-5.4
I <sup>-</sup>	1.41	0.076	-1.3	-3.5

Titratable charge = + 16.8  $\mu\text{C cm}^{-2}$

### Effect of Co-Ion on the Double Layer Charge Distribution

The values of  $\psi_d$  obtained by this procedure for a number of different co-ions are shown in Table 1. Note that although the conductivity of the background electrolyte varies over about 40% the estimates of  $\psi_d$  are fairly constant and, although a little high, are very similar to the 'total' charge derived by titration. This is what would be expected on the basis of the accepted picture of the double layer. The co-ions are repelled from the double layer region and the particular nature of the co-ion would not be expected to have any influence on the distribution. These experiments were done on a polystyrene latex system similar to those for which we had earlier had to introduce this more complicated model of the double layer (Midmore and Hunter, 1987). Only by so doing could we account for the unusual dependence of  $\zeta$ -potential on salt concentration observed with these systems; this anomaly has been under examination for some twenty years past. The present suggestion is consistent with the model presented by Midmore and Hunter (1987). It seems that the problem of anomalous surface conductance is particularly acute in polymer latex systems.

### Effect of Counterion on the Estimated Charge

The effect of changing the cation involved while using the same latex system, is shown in Table 2.

In this case the behaviour of the first four ions is as before. These ions yield a value for the double layer charge which is a little higher than, but comparable to, the titratable charge. For the remainder of the ions, however, the diffuse layer charge is smaller than the titratable charge and it decreases as the ions become more hydrophobic or less well hydrated.

The last three ions are much more likely to be adsorbed to some extent into the compact layer so that the reduction in diffuse layer charge is to be expected. This cannot be taken as definitive evidence of itself, but we do know that latex sols with

these last three ions as counterions are much less stable and more difficult to disperse than when the counterion is of the simple alkali metal type. Again this suggests that the procedure is indeed giving us a measure of the diffuse layer charge.

A similar result is obtained when one uses a number of anionic counterions with a cationic latex (Table 3). The anionic counterions are less well hydrated than the cations and therefore more likely to be adsorbed into the compact layer. Couple this with the higher electrostatic attraction involved in this case (because of the higher surface charge) and it is not surprising that the diffuse layer charge is much less than the titratable charge. The order is the usual 'lyotropic series' which has long been known to characterise the stability behaviour of positive colloids.

### Effect of Temperature on Diffuse Layer Charge

We have examined the complex conductance behaviour of latex dispersions over a range of temperatures from near 0°C to 70°C and again the results are very significant. As indicated in Fig. 3, the value of  $\lambda$  does not change much over that range of temperature and Fig. 5 shows that when translated into terms of diffuse layer charge the change is negligible for well-hydrated alkali cations. These values are again calculated from  $\lambda$

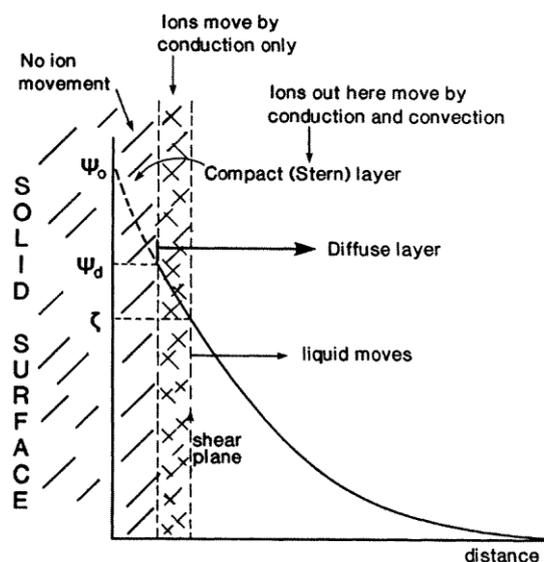


FIGURE 5. The diffuse layer charge at different temperatures for a number of monovalent ions. Note that for the simple alkali metal ions, the charge is constant and similar to the titration charge ( $\int_0$ ) whereas for less well hydrated ions the diffuse charge is much lower. Furthermore, in these latter cases it appears to increase with increase in temperature.

using the Bikerman equation to estimate  $\int_d$  after correcting the electrophoretic mobility for anomalous surface conduction effects. Note, however, that there is some evidence of adsorption into the compact layer ( $\int_d < \int_0$ ) for the less well hydrated caesium ion. The degree of adsorption decreases with increase in temperature as one would expect. The tetramethylammonium ion exhibits the same behaviour to an even greater extent, again as would be expected.

## Behaviour of Ultrasonic Waves in a Colloidal Suspension

A closely related phenomenon occurs when a high frequency sound wave passes through an electrolyte solution or a colloidal suspension. The sound wave causes relative motion of the ions or particles with respect to the surrounding water, assuming they are of different densities. The magnitude and phase of the displacement depend on the charge and inertia of the suspended matter compared to the fluid they displace. A pair of electrodes placed in the solution will pick up an electrical potential which reaches a maximum when the electrodes are at a spacing corresponding to an odd number of half wavelengths. (The wavelength of sound in water at 1 MHz is of the order of a couple of millimetres.) The process was first studied in electrolyte solutions by Debye (1933) and it became known as the *ionic vibration potential*. For ions, the effect is produced by the differences in the mass and frictional coefficients of the ions causing the cations and anions to be differentially displaced by the wave.

The theory was extended to colloidal systems by Hermans (1938). In this case the *colloid vibration potential* or C.V.P. is much larger because much of the charge is carried by the large particles which are displaced much less readily than their countercharge. As the wave passes through the suspension, the double layer charge is displaced with respect to the particle, generating a dipole. There is an obvious similarity here to the effect of an applied electric field (Fig. 2). Extensions to the ultrasonic theory by Booth and Enderby (1952) have been tested by Yeager *et al.* (1953).

Again, our own work is based on the more recent theoretical analysis of Richard O'Brien, which corrects some errors made in the earlier work. New and improved ultrasonic techniques introduced by the Matec Corporation (Mass. U.S.A.) enable us to determine the colloid vibration potential as well as the reciprocal phenomenon: the acoustic wave which is generated when an electrical potential is applied to a colloidal suspension. This latter was discovered and patented by Matec and is called the ESA effect (for Electrically Stimulated Acoustic wave.)

O'Brien (1988) has shown that the two effects are indeed intimately related and that either can be used to determine the particle mobility and hence, the charge. The mobility at these high frequencies is not quite so large as it is at low or zero frequency but it is significant. According to O'Brien it falls to about half of its zero frequency value by the time the frequency has reached about 10 MHz. Our task on the experimental side has been to relate those estimates of high frequency  $\zeta$ -potential to the estimates made at low or zero frequency and so to test the validity of O'Brien's analysis.

### The Measurement System

Fig. 6 shows, very crudely, the principle of the Matec instrument. An electrical pulse of high frequency (1 MHz) and short duration is applied to a piezo-electric crystal and the resulting sonic wave pulse travels down the polystyrene delay rod. By the time the pulse reaches the suspension, the electrical driving signal has disappeared, so the electrodes in the suspension are able to detect the much smaller signal produced by the electro-acoustic effect without interference.

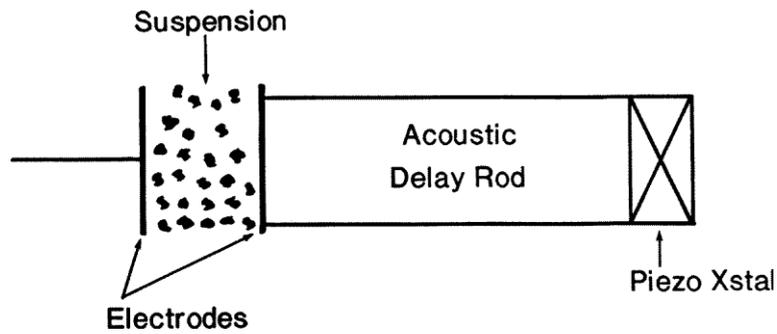


FIGURE 6. Illustrating the general principle of operation of the Matec Electrosonic Analysis apparatus.

The magnitude of the signal is directly related to the electrical charge on the particles and O'Brien's analysis enables it to be estimated accurately instead of relying on a correlation derived empirically from measurements on other systems of known charge.

Another feature of the instrument is that the phase relationship between the applied acoustic wave and the resulting electrical signal undergoes a shift of  $\pi$  radians when the system changes from being positively to negatively charged (Fig. 7). The instrument

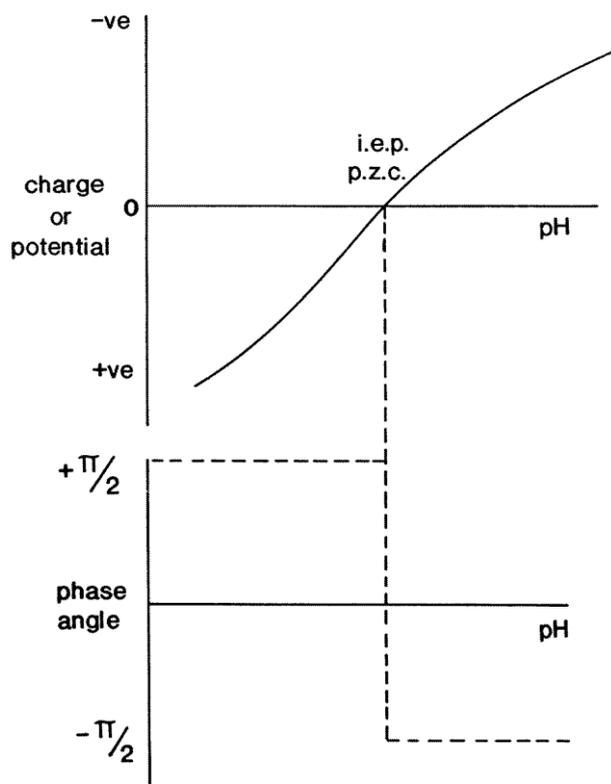


FIGURE 7. The phase relation between the applied electric field and the resulting sonic wave changes abruptly at the i.e.p., which is close to the point of zero charge in many cases. This change can readily be detected in the Matec instrument.

can provide a very precise estimate of the *iso-electric point* of the colloid, by detecting the pH value at which the phase inversion occurs. For many systems, this is the same

as the *point of zero charge*, provided there are no specifically adsorbed ions present. The ease with which these important colloid parameters can be determined by this apparatus is one of its prime features.

### The Critical Time Scales Involved

We have alluded already to the time scale for relaxation of the double layer (Fig. 2). This relaxation occurs in times of order  $\Sigma/K^\infty$  which, for  $10^{-3}$  M KCl, is about 1 microsecond. The time scale for the particle to acquire its limiting velocity under the influence of the field is  $a^2/\eta$  where  $\rho$  is the density and  $\eta$  is the viscosity of the suspension medium. It is interesting to note that this too is around 1 microsecond. By comparison, the time taken to set up the steady state ion density distribution around the particle is much longer, of the order of 1 millisecond. The earlier, lower frequency work has been concerned mostly with that latter process. By moving to the megahertz frequency range, some simplifications can be introduced and although the theory is still rather formidable, some very useful results can be obtained.

### O'Brien's Analysis

The theory shows that the colloid vibration potential should be given by

$$\text{C.V.P.} \propto \frac{|\mu_e| \omega \varphi \frac{\Delta\rho}{\rho} F \left[ \frac{\omega L}{c} \right]}{K^*} \dots\dots\dots (6)$$

where  $K^*$  is the complex conductivity,

$\omega$  is the frequency,

$\Pi$  is the particle volume fraction,

F is a geometric factor depending on the cell length L and the velocity of sound c

$\mu_e$  is the mobility which, at these frequencies, is a complex quantity and the C.V.P. depends on its magnitude.

The electrically stimulated acoustic (E.S.A.) wave has an amplitude which is proportional to the product of the C.V.P. signal and the complex conductivity. It is obvious from equation (6), then, that the E.S.A. signal can be used to estimate  $\mu_e$  without knowledge of the conductivity of the sample.

Once  $\mu_e$  is known at any frequency, it can be used to calculate the  $\zeta$ -potential and charge in the usual way.

### Experimental Testing of the Theory

Fig. 8 shows the effect of particle volume fraction on the C.V.P. signal at various values of background electrolyte concentration. The behaviour is obviously linear up to at least 10% volume fraction.

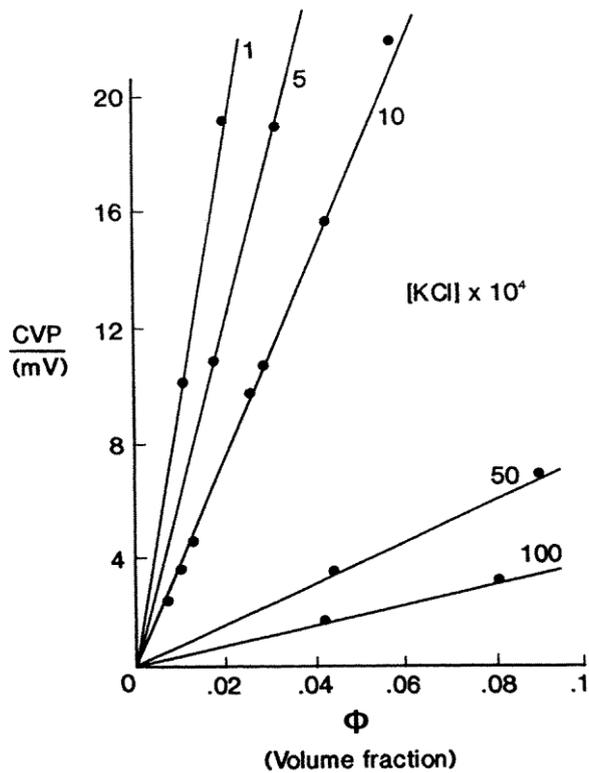


FIGURE 8. Dependence of the C.V.P. on volume fraction at a number of salt concentrations.

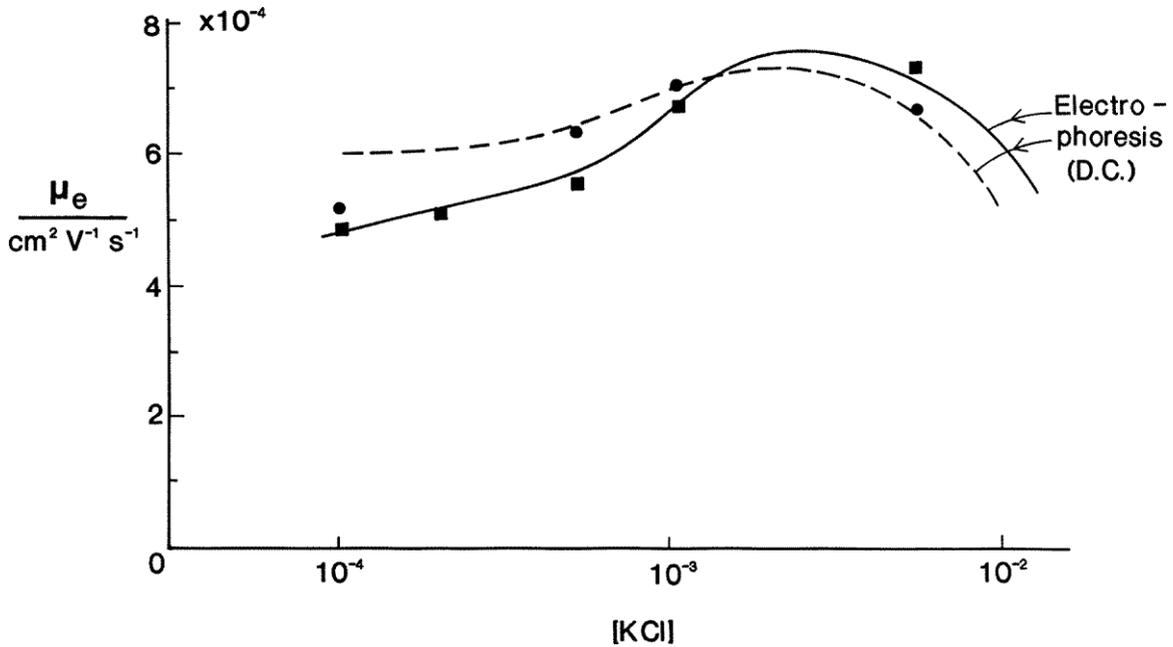


FIGURE 9. Comparison of the electrophoretic mobility measured at high frequency with the corresponding quantity evaluated under d.c. conditions. The surface conduction parameter is assumed to be zero in each case. Full line: Latex M ( $a = 0.88 \mu\text{m}$ ), broken line: Latex 5 ( $a = 1.2 \mu\text{m}$ ). Points are obtained from high frequency measurements after correction for inertial effects.

Fig. 9 shows a comparison between the values of mobility obtained at zero frequency (marked x) and the estimates of  $|\mu_e|$  obtained from the theory after

correction for the inertial effects induced at high frequency. The agreement achieved here assumes that the surface conductivity parameter  $\kappa$  is zero. When the experimental value of  $\kappa$  is introduced, the agreement is much less satisfactory. Just why these systems should appear to behave as though they had no surface conduction is, as yet, unclear.

### Summary

The combination of low frequency conduction behaviour and electrophoresis enables us to determine the diffuse layer charge. This has previously been a very difficult quantity to estimate, yet one which is of great importance since it is the parameter which is needed to calculate the electrostatic interactions between colloidal particles.

Measurements of high frequency conduction and electro-acoustic effects enable us to determine the high frequency mobility. From this quantity it should be possible to determine the  $\zeta$ -potential and charge of colloidal systems in opaque suspensions and at particle concentrations much higher than is currently the case.

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