

## ELECTRICAL DOUBLE LAYER IN SURFACE AND COLLOID CHEMISTRY

AN informal discussion of the Faraday Society on the electrical double layer, particularly in relation to colloid and surface chemistry, was held in the New School of Chemistry of the University of Bristol during September 21-22. The meeting was attended by 129 people, 57 of whom came from industrial organizations and 72 from academic institutions. There were 22 visitors from overseas.

The chair for the session on September 21 was taken by Prof. D. H. Everett (University of Bristol). After a brief welcome to the visitors by Prof. Everett, Dr. R. Parsons (University of Bristol) opened the scientific sessions with a lecture which reviewed the history, and attempted to assess the importance, of the influence of the discrete nature of the charges on the structure of the electrical double layer. He distinguished the effects on the diffuse layer, originally suggested by Frumkin<sup>1</sup> and later developed by Stillinger<sup>2</sup> and Levich and Krylov<sup>3</sup>, from the effects on the compact part of the double layer, which can be traced back to de Boer<sup>4</sup> and which have been worked out in more detail by Esin and Shikov<sup>5</sup>, Ershler<sup>6</sup>, Grahame<sup>7</sup>, Levich<sup>8</sup>, Levine<sup>9</sup>, and Macdonald and Barlow<sup>10</sup>. The uncertainties which exist in these models, that is, the role of the solvent, the effectiveness of the imaging by the outer Helmholtz plane, etc., were mentioned. The importance of devising critical experiments to test these models was emphasized.

Drs. S. Levine (University of Manchester), J. Mingins (Unilever, Port Sunlight) and G. M. Bell (Chelsea College of Science and Technology) discussed, in terms of the discrete ion effect, a number of phenomena at charged interfaces which at present appear inconsistent with the classical Gouy-Chapman-Stern double-layer theory. These authors found that application of the discrete ion theory gave approximately constant values of specific adsorption energy with variation of surface charge, predicted a maximum in the potential at the outer Helmholtz plane with increase in primary charge at fixed ionic strength in the electrolyte, and explained the decrease in concentration of electrolyte required for flocculation of hydrophobic sols with increasing surface charge density. A satisfactory explanation could also be obtained for the phenomenon of mutual antagonism encountered in the flocculation of sols with mixed electrolytes.

The results of potentiometric investigations on the electrical double layer at the silver iodide crystal-solution interface were described by Prof. J. Lyklema (University of Wageningen, Netherlands). The double-layer properties of the silver iodide interface were compared with those of the mercury interface, and the differences and similarities discussed. Adsorption of cations on a negatively charged silver iodide interface was found to be considerably larger than on mercury, probably owing to specific effects. Evaluation of the ionic components of charge at a given potential showed that the adsorption of cations increased in the lyotropic order; a sequence which was also reflected in the flocculation values and in ion exchange. An interesting feature was that the negative adsorption of co-ions did not level off to a given value, as it does on mercury, but passed through a maximum.

Drs. J. J. C. Oomen and Prof. J. Th. G. Overbeek (University of Utrecht, The Netherlands) described measurements of the impedance of silver iodide electrodes, in aqueous solution over a range of  $pI$  and electrolyte concentrations, at frequencies in the range 120 c/s-6,000 c/s. The double-layer capacities of the silver iodide-solution interface obtained using this technique turned out to be very large and dependent on frequency. An

explanation was advanced in terms of surface roughness, and it was shown that on this basis the impedance of the electrode at low frequencies would reduce to a frequency independent series combination of a resistance and a capacity. Experimentally a linear dependence of the square root of the frequency was observed and the differential capacities extrapolated to zero frequency paralleled those obtained with silver iodide suspensions using the potentiometric technique. The ratios of the micro-area to the macro-area were found to be in the range 4-5.

The chairman for the second session, held on September 22, was Prof. J. Th. G. Overbeek. The session commenced with a theoretical paper by Dr. P. H. Wiersema (University of Utrecht, The Netherlands) on the relationship between the electrophoretic mobility and the zeta-potential of a spherical colloid particle. Earlier work on this problem by Overbeek<sup>11</sup> and Booth<sup>12</sup>, which had taken into account both electrophoretic retardation and the relaxation effect, had given approximate analytical expressions for mobility as an incomplete power series in terms of zeta-potential, with coefficients which were functions of  $\kappa a$ ;  $1/\kappa$  is the Debye-Hückel double-layer thickness and  $a$  the radius of the particle. The present work used a numerical solution which corresponds to the complete power series. The differences between the approximations and the present results were appreciable in the region of  $\kappa a$  between 0.2 and 50, and it appeared that the earlier treatments had over-estimated the relaxation effect.

Dr. R. H. Ottewill and Mr. J. N. Shaw (University of Bristol) described an experimental investigation on the electrophoresis of spherical colloidal particles in media of different ionic strengths. Polystyrene latex particles which had been prepared by means of an emulsion polymerization method were used for the investigations; the charge of the particles originated from carboxyl groups on the surface. Five monodisperse preparations were examined with diameters ranging from 600 Å to 4230 Å. Electrophoretic measurements were made using both moving boundary and ultramicroscopic electrophoresis in a range of concentrations of 1:1, 1:2 and 1:3 electrolytes. When examined as a function of  $\kappa a$ , the experimental mobilities gave curves which were qualitatively of the form predicted theoretically by Overbeek<sup>11</sup>, Booth<sup>12</sup> and Wiersema<sup>13</sup>. However, even using the more complete treatment of Wiersema some difficulties were experienced in evaluating zeta-potentials for particles of high mobility with  $\kappa a$  values in the range of 1-10.

Simultaneous measurements of the thickness and conductivity of isolated black foam films were reported by Drs. J. S. Clunie, J. M. Corkill, J. F. Goodman and C. P. Ogden (Procter and Gamble, Ltd., Newcastle upon Tyne). Films having the shape of open rectangular prisms were drawn from solutions of decyltrimethylammonium decyl sulphate, containing sodium bromide (varied from 0.0005 to 0.5 M), and 3-(dimethyl hexadecylammonio)-propane-1-sulphonate, containing sodium bromide (varied from 0.0005 to 1.0 M). The conductance of each film was measured parallel to the surfaces using bright platinum rectangular electrodes and a screened a.c.-bridge. At the limiting film thickness the conductivity measurements indicated an apparent excess of electrolyte in the film core as compared with the bulk solution from which the films were drawn. An explanation of the experimental data was given in terms of Bikerman's theory of surface conductance<sup>14</sup>, and application of Bikerman's equations led to a zeta-potential of about 50 mV for the surface layer/film core interfaces in both systems.

Drs. B. A. Pethica, M. M. Standish, J. Mingins and D. H. Iles (Unilever, Port Sunlight) introduced prelimi-

nary results designed to test the various assumptions made in the thermodynamic theory of the Volta effect. The critical analysis of these assumptions given by Koenig<sup>15</sup> was closely followed. The results were obtained using a vibrating plate electrometer and depended on measuring the compensation potential at the air/electrolyte solution interface in the presence and absence of various spread monolayers. The variation with applied field of the true surface potential ( $\Delta\chi$ ) for some phospholipid monolayers in the zwitterionic form was shown to cast doubt on the general validity of the Bridgman assumption. Within experimental error, the compensation potential does not vary with the separation of the vibrating plate and the solution surface. The Lorentz-Kelvin and Kelvin assumptions though not directly disproved can only be fortuitously correct in particular cases. Tentative proposals for the orientation of water molecules at the solution surface were made.

D. A. HAYDON  
R. H. OTTEWILL

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## NEW BRITISH ANTARCTIC BASE

A SMALL scientific exploration team from the British Antarctic Survey base at Halley Bay has established a research base in unexplored territory 170 miles south of Halley Bay and about 800 miles from the South Pole.

Sir Vivian Fuchs, director of the British Antarctic Survey, who led the Transantarctic Expedition in 1955, stated recently in London that: "This journey into entirely new territory has not only made possible a valuable contribution to ionospheric studies, but has paved the way for a future journey to link up our mapping programme with the work done further south by the Transantarctic Expedition".

The six-man team, led by Dr. G. Bowra, field leader, and Mr. W. Bellechambers, chief scientist, have established themselves at 77° 57' S., 24° 48' W., and have set up an ionosonde to measure the height and density of electrons in the ionosphere between 60 and 250 miles above the surface. Their main object will be to measure the drift of electron clouds over the Antarctic.

The new station, which will be a summer base, was reached after a difficult and hazardous 13-day journey over the ice field in two snow tractors, towing sledges. One of the sledges carried a 'caboose' housing scientific equipment. The equipment is powered by light-weight Villiers 'Mini-Gen' generators, giving about 1 kW of power.

Mr. Bellechambers heads a team of young scientists, mainly from the University College of Aberystwyth, who

are spending two years in Antarctica as part of the British contribution to international research during 1964-65 (designated International Years of the Quiet Sun).

The area in which the British team is working is of particular scientific interest because it is at a very high geographic latitude (so that the Sun does not set for several months in the Antarctic summer) but at a low magnetic latitude. This means that the relation between the ionosphere, the magnetic perturbations, the aurora and the meteorology of the high atmosphere are relatively simple. Such extreme relations between these factors are not found elsewhere in the world.

The Halley Bay equipment for studying the ionosphere includes ionospheric absorption measuring equipment belonging to the Department of Scientific and Industrial Research, an ionosonde and other equipment, some of which is used in co-operation with the United States base at the South Pole.

The team which established the new base consists of: Dr. G. Bowra, field leader and medical officer, Springfield, Ashted Park, Ashted, Surrey; Mr. W. Bellechambers, senior scientist, 40 Hilltop Road, Whyteleafe, Surrey; Mr. L. Dicken, physicist, Dunedin, 18 Risca Road, Rogerston, Newport, Mon.; Mr. P. C. Goodwin, meteorologist, Haughton House, Humshaugh, Hexham, Northumberland; Mr. G. A. Thompson, tractor driver-mechanic, Hope House Cottage, Ettrick, Selkirkshire, Scotland; Mr. B. Kraehenbuehl, Angaston, South Australia.

## GEOLOGICAL EXPEDITION TO CAPES DYER AND SEARLE, BAFFIN ISLAND, CANADA

By PROF. J. TUZO WILSON, O.B.E.\*, and D. B. CLARKE

Institute of Earth Sciences and Department of Geological Sciences, University of Toronto

THE occurrence of Upper Cretaceous and early Tertiary lava flows and sedimentary beds on the Atlantic coasts of Scotland, East and West Greenland, and of similar, but younger, rocks on intervening islands led to the expectation that such rocks might be found in North America<sup>1</sup>. Small patches of Tertiary sedimentary rocks have long been known on the coasts of Ellesmere Island and Northern Baffin Island<sup>2</sup>. In 1952, flat-lying

lavas of undetermined age were photographed at Cape Searle at latitude 67° 12' north on the east coast of Baffin Island<sup>3</sup>. They were later briefly described<sup>4</sup>.

This discovery has special significance in view of A. Wegener's hypothesis<sup>5</sup> that Greenland and northern Canada were separated by the spread of Baffin Bay accompanied by transcurrent faulting along the straits between Ellesmere Island and northern Greenland, and J. T. Wilson's corollary suggestion<sup>6</sup> that a branch of the

\* Present address: Churchill College, Cambridge.