

are equally complicated, and sensitive particularly to the content of amylose. The yield values and apparent viscosities of lutings used for water-proofing screw-threads—for example, a dispersion of synthetic wax in polyisobutene of low molecular weight—have been measured by W. A. Dukes (Ministry of Supply) in the parallel-plate, torsional and cylinder plastometers, with results which are not easy to analyse.

A novel departure from the conventional dispersion was demonstrated by T. C. Daniels (University College of Swansea), who described experiments on the fall of metal spheres of different sizes and densities through fluidized beds of sand, ilmenite, and similar powders. Such a bed is not a single, physically well-defined piece of matter but consists of a 'framework' of dispersed particles with the continuous component (air) in appreciable linear motion relative to this framework. The usually neglected migration effects (sedimentation, creaming, etc.) are here of great importance. Anisotropy is to be expected because of the privileged direction of the air flow. Experimental results lead to an empirical law that the terminal velocity of fall of a sphere through the bed is a constant plus a term proportional to diameter squared and to a power (somewhat greater than unity) of the density difference. Such a clear departure from Stokes's law deserves the interest of theoreticians. The experimental work is to continue with an investigation of the viscosity appropriate to shearing between vertical cylinders.

Informal evening discussions in the recently opened men's hall of residence, Neuadd Gilbertson, included one at some length on the subject of rheological nomenclature, to which much thought had been given by the Dutch rheologists. A free exchange of widely divergent views, under the chairmanship of Dr. G. W. Scott Blair, brought into relief, if nothing else, the many different scientific disciplines—physics, biology, engineering, chemistry, mathematics—which are brought together in the membership of the British Society of Rheology for the study of deformation and flow.

## HIGH POLYMER, COLLOID AND SURFACE CHEMISTRY

UNDER the auspices of the South Australian Branch of the Royal Australian Chemical Institute, a discussion meeting on "High Polymer, Colloid and Surface Chemistry" was held during August 19–21 in the Department of Physical and Inorganic Chemistry at the University of Adelaide. The meeting was arranged by the Theoretical Chemistry Group, which has felt for some time that, because of the isolation due to the large distances between centres of research in Australia, there exists a great need to bring together members working in related fields of chemistry so that current problems can be discussed.

More than seventy members and visitors attended, including forty visitors from other States of the Commonwealth, and twenty-nine papers were presented during the three-day meeting. These were classified under the general headings: surface chemistry; synthetic high polymers; and poly-electrolytes and natural high polymers. The session opened with a series of papers dealing with the

measurement and interpretation of surface phenomena.

The first paper, by Prof. A. E. Alexander (University of Sydney), outlined the methods employed in studying the relation between surface mechanical properties and chemical constitution of linear polymers. Prof. Alexander reported on a recent examination of isotactic and atactic polypropylene oxide at the oil/water interface. The necessity for further study at lower surface pressures was stressed. Some aspects of the surface properties of co-polymers consisting of styrene with very small amounts of vinyl pyridine were discussed.

Dr. C. S. Hocking (Imperial Chemical Industries, Australia and New Zealand, Melbourne) described some investigations by himself and Miss G. M. Parkins into the effect of changes in the degree of hydrolysis and molecular weight of polyvinyl alcohols on surface properties. A series of commercial polyvinyl alcohols, varying from 73–98 per cent hydrolysed, had been examined.

The use of ultra-violet absorption spectra in determining critical micelle concentrations of solutions of alkyl pyridinium iodides in water and organic solvents was reported by Dr. J. A. Friend (University of Tasmania). Above the critical concentration of micelles in water new absorption bands appear and are considered to be due to the iodide/pyridinium association. There was much discussion concerning the manner in which the iodide ions are associated.

A paper by D. A. Haydon and J. N. Phillips on the adsorption of detergents on oil drops and their charge/potential relationship was read by Dr. Phillips (Commonwealth Scientific and Industrial Research Organization, Canberra). His results confirmed that the theoretical form of the Gibbs equation is applicable to the adsorption of surface-active electrolytes in the absence of an additional electrolyte. The adsorbed ions obey the equation of state for an ideal charged monolayer. No simple relation was found between the surface and zeta potentials.

In a paper by J. N. Phillips and N. A. Walker (Commonwealth Scientific and Industrial Research Organization, Canberra) on the effect of detergents on *Nitella* cells, Mr. Walker showed evidence which suggests that the site of attack of solutions of both cationic and anionic detergents on cells of the green alga *Nitella* is the cytoplasmic outer membrane. The time required for death of cells to occur was studied. The relative effects of detergents and of changes in salt concentration indicate that adsorption on a negatively charged surface is involved. Adsorption of the detergent on the cell wall has been investigated.

Dr. B. S. Harrap (Commonwealth Scientific and Industrial Research Organization Wool Textile Research) presented the results of a study of the surface properties of soluble derivatives of wool keratin. Surface properties of the dye 'orange II' were described and also the influence of pH and ionic strength on the interaction of the dye with monolayers of a partially fractionated soluble derivative of wool keratin. At low ionic strength, interaction is probably by ionic bonding between dye anions and positively charged protein side-chains below the interface. At high ionic strengths, penetration of the monolayer by the dye is apparent. This is due to a change in the state of the dye adsorbed at the interface.

Surface films of gluten have been investigated, and surface pressure, compressibility, viscosity and

rigidity at both air/water and oil/water interfaces have been measured. Mr. N. W. Tschoegl (Bread Research Institute of Australia) pointed out that the decision to use the techniques of surface chemistry was dictated largely by their cheapness. The systems studied were solutions of gluten in hydrochloric acid, sodium salicylate and mixtures of hydrochloric acid in ethylene chlorhydrin.

The adsorption of high polymers on solids was reviewed by G. E. Neu (New South Wales University of Technology), who pointed out that very little work had been done on the subject. Mr. Neu reported that the system polyvinyl acetate/carbon black/benzene is being investigated in Sydney, where the amount of polymer in the solvent is estimated by means of measurements of surface pressure.

Dr. B. D. Cuming (Commonwealth Scientific and Industrial Research Organization, Melbourne) discussed the adsorption of amphipathic ions on an ionic solid. The theory proposed by Held (1935) has been shown to account for the re-wetting of the surface at high concentrations. Measurements of adsorption of sodium dodecyl sulphate on barium sulphate and the effect of potential-determining and other ions are supported by the double-layer theory.

The rate of desorption of radioactive stearic acid, deposited by the Langmuir-Blodgett technique on single and polycrystalline silver surfaces, have been measured by Geiger-counter and autoradiographic techniques. J. A. Spink (Commonwealth Scientific and Industrial Research Organization, Melbourne) described experiments which show that the forces by which long-chain polar molecules are attached to solid surfaces depend upon the crystal orientation of the substrate. Since desorption rates have also been found to be influenced by the state of surface, it was necessary to standardize the method of surface preparation.

The first two papers on the second day were concerned with kinetic studies. In the first, Dr. A. Parts (University of Sydney) presented some results on the kinetics of polymerization of acrylonitrile in water in the presence of hydrogen peroxide and ferric salts. The reaction was found to be second order with respect to the dissolved monomer. The rate increases with increasing concentrations of hydrogen peroxide and iron salt, but decreases with increased concentration of hydrogen ions. The degree of polymerization was found to increase with increasing concentration of monomer and hydrogen ions, but to decrease with increasing concentration of hydrogen peroxide and ferric salt. Possible mechanisms were discussed, but the complete picture remains obscure.

In the second paper some recent work on the polymerization of styrene in solution in carbon tetrachloride and catalysed by aluminium chloride was reported by F. E. Treloar (University of Adelaide), who stated that intensive drying of reagents failed to stop polymerization. However, the bright colours attending the reaction indicate that the last trace of water was not completely eliminated. The rate of polymerization was shown to be second order with respect to the monomer and first order with respect to the catalyst.

The two papers on kinetics were followed by a group of three papers dealing with synthetic problems concerning block and graft co-polymers. Presenting the first of these papers by W. G. P. Robertson and J. M. Hammond, Mr. Hammond (Weapons Research Establishment, South Australia) described several methods

attempted in the synthesis of polymers consisting of a polyisobutene backbone bearing branches of poly-methyl acrylate. The most successful involved conversion of the hydrocarbon polymer to a photochemical polyinitiator by photobromination, followed by branch-growth polymerization of methyl acrylate. The graft polymers formed display odd behaviour in solution due to the marked difference in nature between the backbone and the branches of the molecules. Kinetic study was hampered by troubles with solubility, but it was obvious that the kinetics of the system are more complicated than might be expected.

Two new methods for preparing block co-polymer were presented by Dr. J. R. Urwin (University of Adelaide). In the first case, polystyrene containing cumenyl end-groups was prepared by polymerizing styrene in the presence of cumenyl mercaptan. The polystyrene was oxidized and the product used in an emulsion-type polymerization of methyl methacrylate. In the second case, the dihydroperoxide of cyclohexanone was used in an emulsion polymerization to produce polystyrene, which was then employed as an initiator in the bulk polymerization of methyl methacrylate. The polymers were shown to contain block copolymer by comparing the turbidimetric titration of the block with simple mixtures of the parent polymers.

The third paper, presented by D. H. Solomon (Balm Paints, Sydney), described how the application of concepts of polymeric structures of block or graft type were contributing to the evolution of improved surface coatings. Blends of alkyds, drying oils, vinyl monomers with epoxy and urea formaldehyde resins have shown that some of the resulting three-dimensional structures with long-range periodicities offer outstanding combinations of desirable properties.

Of technological interest also was the next paper, on the cross-linking efficiency of monomers in polyester resins, by W. G. P. Robertson and D. J. Shepherd (Weapons Research Establishment, South Australia). In the paper, read by Dr. Robertson, the physical properties of resins prepared from the same unsaturated polyester with different monomers were compared. Some correlation was found between resin properties and calculations of degree of cross-linking based on the known behaviour of the monomers co-polymerized with fumarate esters.

Dr. J. V. Sanders (Commonwealth Scientific and Industrial Research Organization, Melbourne) read a paper by himself and R. G. Sherwood on the thermodynamics of mixtures of silicones and benzene. Measurements have been made of the vapour pressures of these mixtures over the complete range of concentrations. Results were compared with calculations made using the 'cell' theory of liquids and the agreement was found to be satisfactory. Three samples of silicones available commercially, with the usual spread of molecular weights, were used in these experiments.

In a study of second-order transitions in non-crystalline high polymers Dr. H. A. J. Battaerd (Imperial Chemical Industries, Australia and New Zealand, Melbourne) presented the results of a study of apparent second-order transitions in the system polyvinyl chloride/dioctyl phthalate, made by following the dependence of refractive index on temperature. A number of transitions were found, suggesting various stages in the plasticization.



I. Endzins (Hilton Hosiery, Ltd., Victoria) described the fractionation of three commercial acetate rayons in the system phenol/cyclohexane. The mass, frequency and integral distribution curves were determined. The relations between these distributions and such properties of the fibres as acid content, swelling and absorption of moisture were discussed.

The final day was devoted to discussion of polyelectrolytes and natural high polymers. The first two papers concerned properties of solutions of polyelectrolytes, and then a series of papers on natural high polymers was read. Studies of viscosity, conductance and streaming birefringence in aqueous solutions of poly-4-vinyl pyridonium chloride were presented by T. Kurucsev (University of Adelaide). The dependence upon concentration of these physical properties was found to be discontinuous at very low concentrations, and an interpretation of this behaviour was presented in terms of the reversible aggregation of the polyelectrolyte molecules. The possible forces involved in the formation of aggregates were discussed.

Experiments designed to measure the charge on polyelectrolytes in solution were described by J. E. A. Gooden (University of Adelaide). It was reported that measurements of conductivity and of transport properties on polymethacrylate ions showed a decrease in charge with an increase of bound counterions. Sodium deoxyribonucleic acid shows the opposite trend. It was suggested that a composite curve of these results might in fact represent a general phenomenon.

The denaturation of proteins by the action of urea was reviewed by Dr. H. A. McKenzie (Commonwealth Scientific and Industrial Research Organization, Sydney). The results of experiments on a series of proteins in the presence of 7 *M* urea were discussed in terms of a denaturation process and aggregation. Measurements of sedimentation, diffusion and viscosity had been used for determining denaturation and optical rotation to detect aggregation. Dr. McKenzie reported the effects of *pH* on these measurements, and cautioned against drawing conclusions at a particular range of *pH*, since in some cases reaction is slow and therefore the measurements are dependent upon time.

The interaction of whole serum with water-soluble amides and triazoles in relatively dilute solutions was reviewed by Prof. J. B. Polya (University of Tasmania). The main features of extensive electrophoretic studies were presented in some detail. The effects of time, *pH* and protein concentration were reported, together with preliminary viscosity data. Prof. Polya presented an interpretation of these observations and discussed some applications.

The properties of  $\alpha$ -keratose and S-carboxymethyl keratine-2 have been studied by sedimentation, viscosity and light-scattering methods by E. F. Woods (Commonwealth Scientific and Industrial Research Organization, Melbourne). It was shown that in aqueous buffer systems the molecular parameters determined by these methods are dependent on time, temperature, salt concentrations, *pH*, and time and speed of centrifuging. The influence of disaggregating agents has also been studied. The most effective were 8 *M* urea, sodium dodecyl sulphate, 10 *M* acetic acid and *N*/10 alkali.

Dr. J. M. Creeth (University of Adelaide) read a paper by himself, L. W. Nichol and D. J. Winzor on electrophoretic fractionation of the albumin

component of egg white and the characterization of original and fractionated material by means of measurements of Rayleigh diffusion. The two components apparently had identical coefficients of diffusion. This lends some support to the hypothesis that the only difference between the components lies in their content of phosphate.

A paper by L. G. Ericson and S. G. Tomlin (University of Adelaide) on the study of collagen by means of low-angle X-ray diffraction techniques was read by Dr. Tomlin. This work was designed to give evidence about details of organization in the size-range of, say, 10–1000 Å.—and thus provide information about the arrangements of large molecules in fibrous structures. Attempts to solve the problem of the interpretation of these diffraction patterns by the incorporation of heavy atoms into collagen fibres have been made using the complementary techniques of X-ray diffraction and electron-microscopy. In this way it has been possible to locate heavy atoms in the fibres, and a preliminary account of these findings was presented to the meeting.

In a paper on the sedimentation of nucleic acid solutions, J. H. Coates (University of Adelaide) described experiments which indicate that the very sharp sedimentation boundaries exhibited by solutions of sodium deoxyribonucleate in the ultracentrifuge are related to a change in the charge on the nucleate ion across the boundary. Mr. Coates considered that this explanation is in closer agreement with experimental results than the hypothesis of the dependence of the sedimentation coefficient upon concentration.

R. B. Inman (University of Adelaide) described some results from measurements of conductivity and transport made on salt-free deoxyribonucleic acid. Derived values, such as the charge and mobility of the polyion kinetic unit, were reported at the meeting, and it was suggested that the observed change of properties with concentration results from a reversible equilibrium between single molecules and aggregates.

The isolation of tobacco mosaic virus in various states of aggregation was reported by J. N. Phillips and M. Zaitlin (Commonwealth Scientific and Industrial Research Organization, Melbourne). Preparations of two strains of purified tobacco mosaic virus subjected to continuous electrophoresis on filter paper have been separated into a number of fractions. These fractions were examined by light scattering, by ultra-violet spectrophotometry and in the electron microscope. In the one case ( $U_2$ ) little difference was observed between the fractions, whereas in the other there was a progressive variation in the content of nucleic acid and in average molecular weight. Furthermore, the distribution of particle sizes throughout the  $U_1$  fractions indicated the virus rods were split in a non-random fashion on the paper. These observations were discussed with reference to the different physical behaviour of the two strains in the light of the current conception of the structure of the tobacco mosaic virus.

That the meeting afforded those who attended a welcome opportunity to meet others working in related fields and to discuss current research problems was evidenced by the enthusiasm with which the papers were received and the lively discussion and comment they aroused.

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