Preface

It could well be that prefaces are the least read of the greatly unread productions of modern publishing but the following paragraphs are written to try to help the reader decide what in this particular volume has any claim to his attention. This volume is the first of a new biennial series on dielectric and related studies, so some comments are offered on the area embraced by the title and some of the prospects in this area of molecular science are described. Then the specific characters of the contributions in the volume are briefly indicated, and this could help the reader find those of greatest immediate interest to him. In any case the preface should be helpful to a reviewer.

The term 'dielectric properties' in its broad usage refers to those responses other than the simple ohmic currents which develop in a medium on the application of an electric potential. Thus an ideal dielectric medium shows no direct current when a static electric potential is applied, but as only gases approach this condition it is usual to speak of the dielectric properties of what may also be a semi-conductor.

No material medium is known which can be adequately described as having a 'dielectric constant', *i.e.* polarization which is strictly proportional to the electric field, and independent of its frequency, the temperature, and pressure. Both for general physical and molecular interests the study of dielectric properties becomes the investigation of the variation of the electric permittivity with the several variables to which it responds: thus the study becomes field-dependent dielectric spectroscopy, with the thermodynamic variables of state (concentration, temperature, pressure, *etc.*) as other necessary parameters. Such attempts to define a specific area in the scientific field are certain to fail in practical use by being too narrow or too broad. *Dielectric* spectroscopy necessarily has a very broad frequency range in the electromagnetic spectrum and an arbitrary and appropriately variable limit can be set by confining it to the range of non-quantal interactions of electric fields with material systems. This serves to separate it from most aspects of optical spectroscopy, although a reference to the Maxwell relation, (electric permittivity) = (refractive index)^2, suffices to show this is an artificial border. Also, for present purposes, the magnetic field-dependent aspects should be excluded as they embrace the special topic of n.m.r. spectroscopy. With these exclusions, dielectric spectroscopy may be taken to extend up to frequencies of *ca.* 10^{13} Hz, *i.e. ca.* 300 cm^{-1}.

The range of subject matter and the variety of techniques in this broad area have meant that in the past dielectric studies have tended to develop in almost independent patches and even now—except in some theoretical aspects—a deliberate attempt has to be made to bring the diverse but cognate features together. The emergence of 'materials science' as a recognized discipline embracing aspects of physics, chemistry, and engineering science has hastened the merging of dielectric studies, and von Hippel must be credited with a major pioneering role in this development. In the U.K. the flourishing of a Dielectrics Discussion Group with members from three major scientific disciplines is a significant feature, the more so because as a dielectric study group they do not find it appropriate to be formally associated with any of the established societies to which they otherwise belong. However, this series of volumes, which it is intended will appear biennially, will be concerned primarily with molecular aspects of dielectric studies. This net is already a large one and the Senior Reporter will be happy to consider suggestions from colleagues as to the selection of topics for later volumes.

It cannot be said that this is the first attempt to provide a regular series of reports on progress in dielectrics but, insofar as they continue, some of the earlier ventures are now very irregular in their appearance. At the same time dielectric studies are acquiring increased momentum and range. As symptoms of these features one can mention the arrival of dielectric spectrometers which scan very many decades of frequency to provide an almost immediate spectrum of both the permittivity and absorption changes as functions of frequency. The Reddish–Hyde dielectric spectrometer is certain to initiate a revolution in the measurement of time-dependent properties, as the variation in any bulk property, *e.g.* in chemical composition, density, viscosity, *etc.*, which can be converted into a capacitance change can now be automatically scanned and recorded over times from 10^{-6} s to 10^{3} s. In view of the dominant role which reaction kinetics has had for some decades in British physical chemistry, it is safe to predict that the 1980's will see very many of our laboratories equipped with dielectric spectrometers and the area will receive that accolade of well-established topics, a special committee and allocation of funds by the S.R.C. On the interpretative side, recent years have also seen the replacement of the simple dipole relaxation model of Debye (1913), which provided the pattern of discussion for more than half a century, by the more general representation of the Kubo correlation function. Formally this provides a means of unifying the total time pattern of the changes in a dielectric, be they of single or multiple origins, and independently of the sequential or simultaneous occurrence of the component (model) processes. Finally, and not least significantly, the more than thirty years of pioneering work of Piekara in the study of high electric field effects is now proliferating in a variety of directions, and another prediction is easy: before the end of the century Piekara's work will undergo the same expansion as we have seen in Aston's lone exploitation of the mass-spectrometer.

Coming to the present volume, one aim has been to provide a basis on which the student and researcher in molecular science can build a sound appreciation of the present and future developments. Accordingly, the chapters do not presume too much previous knowledge of their subjects. Professor Scaife is concerned, *inter alia*, to make clear what is the character of those aspects of the macroscopic dielectric behaviour which can be precisely delineated in the theoretical representations which rest on Maxwell's analysis, and he relates these to some of the general microscopic features. The time-dependent aspects of these features are the particular concern of Chapter 2 in which Dr. Wyllie gives an exposition of the essentials of molecular correlation functions. As dielectric relaxation methods provided one of the clearest models of relaxation studies, there is reason to suggest that dipole reorientation provides one of the clearest examples of the correlational treatment. If only for this reason, Dr. Wyllie's chapter could well provide valuable insights for many whose primary interest is not in dielectrics.

The gas phase is invariably regarded as the simplest for a quantitative representation of molecular behaviour, and undoubtedly the dilute gas is one where the Debye treatment in terms of the dipole moment receives its best justification. Despite the century-old insights of van der Waals on the gas deviations which so strikingly help in appreciating the appearance and behaviour of the liquid state, the parallel links in our understanding of the dielectric behaviour of liquids have still to be forged. In Chapter 3 Dr. Sutter summarizes the present analysis of the permittivities of gases at higher pressures. Their study serves to reveal some of the essential detail in two- and three-molecule encounters. Furthermore, the difficulties, both experimental and theoretical, in the dielectric appraisal are explicitly illustrated, and much if not all of the currently valid molecular data from this source are summarized in the account.

It is a trite observation that our understanding of water is in many respects even less adequate than that of other liquids. Recent monographs have shown that the past decade has seen significant advances, but a satisfactory treatment of the dielectric spectrum is still elusive. Professor Hasted, who has long-developed interests in this problem, contributes his own assessment of the present situation in Chapter 4. He includes an account of some computer-model calculations as well as a summary of recent far-i.r. observations which are of immediate relevance to the quantitative appreciation of the dielectric spectrum of water.

The newly established methods in time-domain dielectric studies are reviewed by Dr. Suggett in Chapter 5. In general principle these are extensions of the step- or ramp-voltage methods which in various forms have been in occasional use over some thirty years, but the differences in the speed of operation are such as to make them qualitatively different. For the high-frequency region the first system was described by Fellner-Feldegg in 1969, whilst a spectrometer operating from 10^{-4} Hz to 10^{6} Hz

was only described in 1970. Accordingly, we are still in the very early stages of these newer methods and many extensions and improvements will certainly follow.

Of special systems, those in the biomolecular field offer a special challenge and also special opportunities. The challenge is many headed: the difficulties of handling small amounts of complex material in conducting (usually aqueous) media are considerable. The largest molecules can acquire some properties of macroscopic particles so that interfacial effects can add to the complications. Furthermore, various intramolecular configurations may not only be present but may be in dynamic equilibrium. Changes in the latter may be equivalent to chemical processes and can often be of the greatest importance in the biological function of these molecules. Professor Schwarz in Chapter 6 has given a systematic presentation of many of these aspects. He deals firstly with conditions under which a meaningful electric dipole moment can be evaluated for a solute species. Accordingly this chapter might well be the first choice for many chemists and biophysicists. In it Professor Schwarz also explains the possible measurement of chemical rate processes in the form of a directly observable dielectric absorption. For the biomolecular scientist the possibilities here must be quite exciting and Professor Schwarz refers to some instances where the possibilities have been realized.

Finally there is Chapter 7 by Professor Kielich which, in fact, might form a small monograph of its own. The introductory survey of this chapter serves to orient the student in the general field of dielectric studies and it provides a selected bibliography for the whole subject which many readers, it is hoped, will find of lasting value. The special aim of the chapter is to outline systematically the present possibilities in high electric field studies both in terms of the macroscopic factors and at the molecular level. This whole new area is ripe for systematic exploration and Professor Kielich has made a major contribution to the prospects in future work by presenting the general theory and much specific detail for several aspects which can already be envisaged. No such survey of high electric field effects has previously been available and many colleagues will be grateful to Professor Kielich for the major effort he has given to this thorough presentation. The chapter includes a number of features which have not been generally expounded: *e.g.* the significance of fluctuating local fields present in condensed vapours and liquids. Few will read the summary contents of Chapter 7 without finding some worth-while items with which they are not familiar.

Such, briefly, is the content of the chapters which follow. Apart from thoroughly recommending them to others, it only remains for this first reader to offer his sincere thanks—not only for the very ready collaboration of the authors, but also for their valuable contributions to the not excessive corpus of significant literature on dielectric studies. The interest and help of the Chemical Society editors are also much appreciated.

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Aberystwyth, May 1972