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THE EFFECT OF VARYING THE POLARITY OF THE SOLVENT ON THE RATE OF CHLORINE-ADDITION TO OLEFINS

CHLORINE-addition to olefins in a moderately polar solvent such as acetic acid is an electrophilic reaction involving neutral molecules of olefin and chlorine as the reactive species[1]. The reaction is thus a typical example of a dipole-dipole reaction. The kinetics of this reaction in acetic acid has been recently investigated by adopting an experimental technique developed earlier in this laboratory for the chlorination of aromatic compounds[2,3]. The significant achievement in these investigations was the fact that the loss of chlorine due to volatility during a kinetic run was extremely low (less than 1%), an accuracy not achieved hitherto by earlier workers. Due to this new experimental technique, accurate kinetic and Arrhenius parameters could be evaluated. In this communication, the effect of increasing the polarity of the solvent (by the addition of water) on the rate of the reaction is reported. It is also shown that an empirical equation, first proposed by Seshadri and Ganesan[4] for a dipole-dipole reaction in solvents of varying polarity, is applicable in the present case.

The kinetics of chlorine-addition to butyl acrylate was studied in various acetic acid-water binary mixed solvents (water content being 0, 5, 10, 15, 20 and 25%)

by volume) at 26° C. For each solvent the second order rate constant (k_2) was evaluated by using the integrated rate equation

$$\log \{b(a-x)/a(b-x)\} = \{k_2(a-b)/2\cdot303\} t$$

as described in the earlier paper[2]. It was found that k_2 increased with increasing water-content (or dielectric constant) of the medium. This trend shows that the activated complex formed during the reaction is more polar than the reactants[5,6].
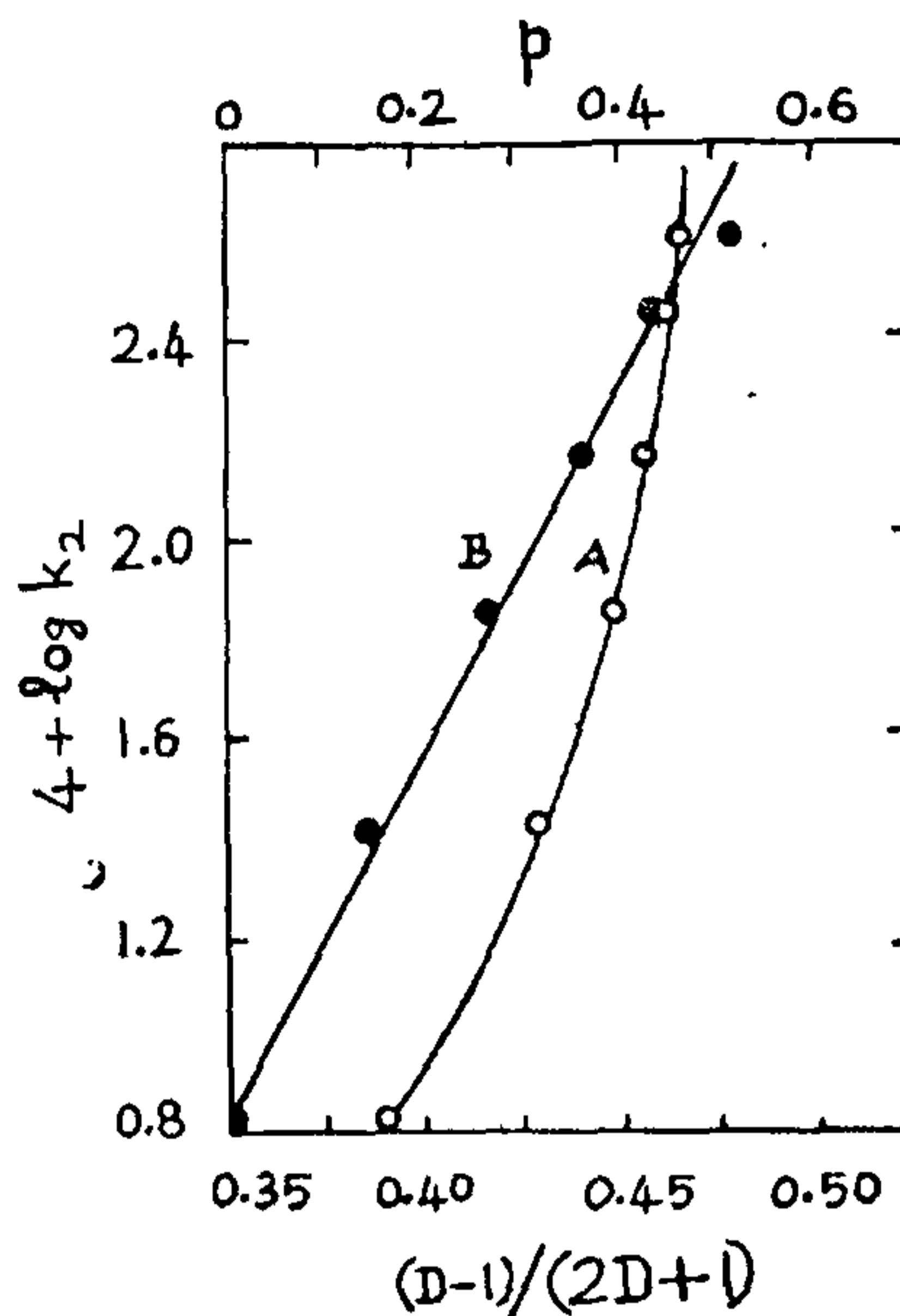

FIG. 1. Chlorine-addition to butyl acrylate in acetic acid-water mixed solvents at 26° C. A. Plot of log k_2 against $(D-1)/(2D+1)$. B. Plot of log k_2 against p.

Figure 1 shows plots connecting k_2 and the solvent properties. The plot of log k_2 against $(D-1)/(2D+1)$ is not linear (plot A), although it is expected to be so for a dipole-dipole reaction[7,8]. However, the limitations of such plots connecting the macroscopic dielectric constant (D) of the medium with the rate constant are very well known[9]. For a dipole-dipole reaction, such as the electrophilic bromination of paradimethoxy benzene in acetic acid-water mixtures, the following empirical equation was first proposed and found to be applicable[4],

$$k_{(aq)} = k_{(dr)} e^{ap}$$

A plot of log k against p was linear. Here $k_{(dr)}$ and $k_{(aq)}$ are the rate constants in dry and aqueous acetic acids, p is the mole fraction of water in the

solvent and a is a constant ($k_{(aq)} = k_{(dry)}$ when $p = 0$). In the present reaction also, a plot of $\log k_1$ against p gives a good straight line (plot B) and thus provides one more experimental verification for the equation proposed earlier. The equation has already been found to be applicable to bromine-addition to methacrylamide[10].

Physical Chemistry Dept.,   R. M. SUBRAMANIAN.
University of Madras,   R. GANESAN.
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FOSSIL ALGAE *SOLENOPORA* AND *AMPHIROA* FROM THE TRICHINOPOLY CRETACEOUS ROCKS OF SOUTH INDIA

STUDY of fossil algae from the Trichinopoly Creataceous rocks by Rao and Gowda[1] and Gowda[2,3] has revealed that the genus *Solenopora* ranges beyond Jurassic in time. That its range is upto Danian is shown by the studies made by Rao and Gowda[1] and Keijzer[4]. Further study of the fossil algae from the same has confirmed the wider range of *Solenopora* through its association with *Amphiroa*. The latter genus is known to range from Upper Albian onwards[5]. Newly found *Solenopora–Amphiroa* association in the Trichinopoly Creataceous region is noticed in the Varagapaudy limestone band that occurs at the base of the Uttatur Group. This band of limestone is one of a series of bands occupying the same stratigraphic position.

The generic identity of *Solenopora* (Figs. A and B) is based on the characteristic irregular arrangement of transverse septa. Similarly the genus *Amphiroa* (Fig. C) is recognised by the larger cells alternating with the smaller cells in the vertical direction. Both genera occur in detached form, as seen in thin sections of the rock.
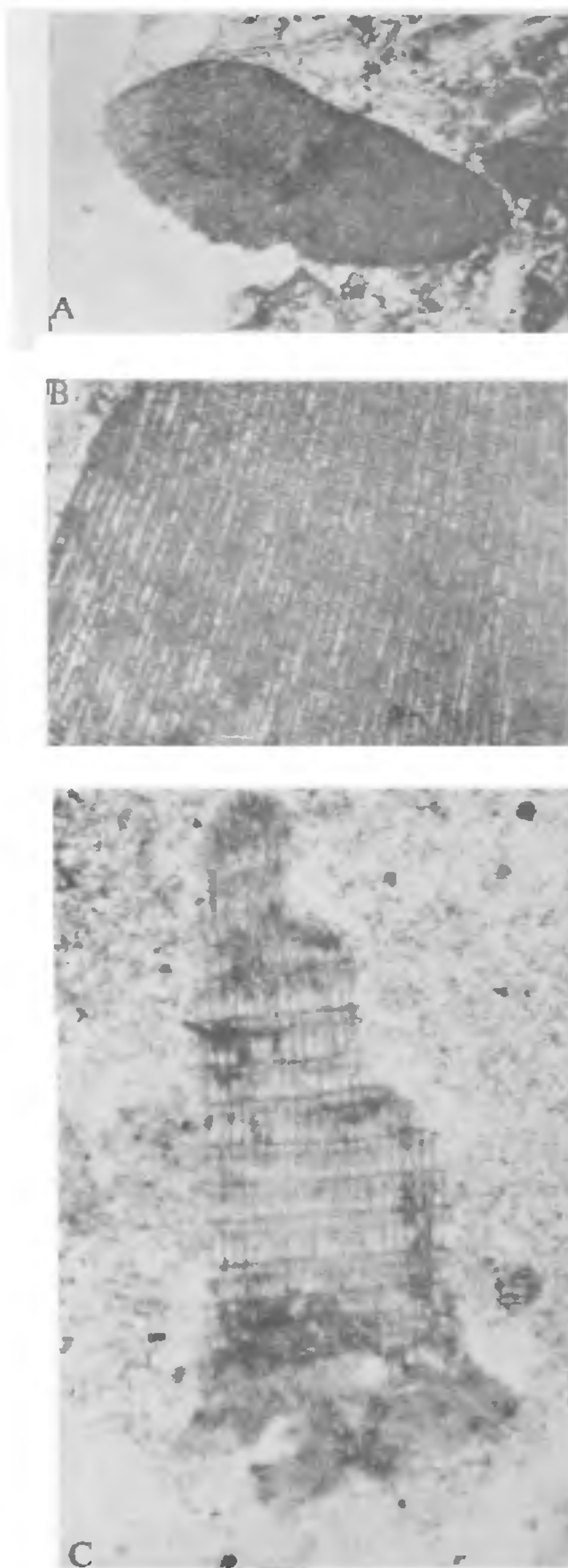
FIGS. A–C. Figs. A and B. *Solenopora* sp., A × 25; B × 50. Fig. C. *Amphiroa* sp., × 100.