DIELECTRIC CONSTANTS AND ASSOCIATION IN DILUTE ETHANOL SOLUTIONS IN CARBON TETRACHLORIDE

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ABSTRACT. — Dielectric constant versus concentration data have been collected for solutions of ethanol in carbon tetrachloride over the concentration range of 0.015 to 0.085 *M*, and the data are presented as an example of the indication of the association behavior in such systems. The resulting curves have been statistically analyzed by computer techniques.

In recent years there have been a number of studies on dielectric properties of solutions of materials which may involve hydrogen bonding. However, most of these studies on alcohols have dealt with solutions varying in alcohol concentration over the entire range of zero to one mole fraction, with few if any measurements reported for dilute solutions containing alcohols in concentrations of less than about 0.10 *M* (Gold and Perrine, 1967A; Gold and Perrine, 1967B; Malecki, 1962; Malecki, 1965; Piekara, 1962). Rodebush, *et al.*, have shown that the total polarization curves for solutions of some alcohols in carbon tetrachloride show a decrease in slope at concentrations where association is considerable (Rodebush, Eddy, and Eubank, 1940). Spectroscopic studies have shown that alcohols are extensively self-associated even at relatively low concentrations in inert solvents (Fletcher and Heller, 1967A; Hammaker, *et al.*, 1968; Fletcher and Heller, 1967B; Van Ness, *et al.*, 1967). Similarly, at intermediate and high concentrations, the alcohols are extensively associated in higher aggregates. Therefore, most of the measurements on dielectric properties of alcohol solutions have been made on solutions in which the alcohols are not involved primarily in a monomer-dimer equilibrium. It has been shown that for the case of some simple alcohols in nonpolar solvents the slope of the dielectric constant versus concentration curve exhibits a less rapid increase in the concentration range dominated by monomer-dimer equilibrium than on either side of this range (Smith, 1955, pp. 303-306).

This report presents, as a specific instance in detail of the above, dielectric constants for solutions of ethanol in carbon tetrachloride at concentrations less than 0.1 *M* and their apparent indication of variations in the predominant equilibrium.

EXPERIMENTAL

Materials. The CCl_4 used as a solvent was washed several times alternately with alcoholic KOH, water and concentrated H_2SO_4 until the washings were colorless. The purified material was distilled from $CaCl_2$ and stored in ground-glass stoppered containers, and all subsequent operations were carried out with the exclusion of moisture. The purified material gave no proton resonance spectrum and showed no absorption in the infrared spectrum in the region where O-H stretching bands are found.

Ethanol was refluxed with metallic sodium or magnesium and vacuum distilled. It was stored in glass stoppered containers kept in a desiccator. The CCl_4 solutions were stored in the dark and were prepared with freshly purified CCl_4 approximately weekly. Standards used for instrument calibration in determining dielectric constants were cyclohexane and chlorobenzene. These materials were freshly distilled spectral grade chemicals.

Dielectric Constant Measurements. Dielectric constant measurements were made using a Sargent Model V Oscillometer. Conversions of scale readings to cell constants and to dielectric constants were programmed. All measurements were made at 25 ± 1°C. Individual dielectric constants are estimated to be accurate to within about ±0.003. The dielectric constant data, as a function of concentration, were examined by a computerized polynomial regression technique.

RESULTS AND DISCUSSION

The dielectric constants obtained for the dilute ethanol solutions are shown in Table I. A plot of the average values given in Table I shows that the relationship of concentration to dielectric constant is not linear but rather has a region of lower slope between about 0.04 and 0.07 *M*. This same behavior was observed for several sets of ethanol solutions other than those for which measurements are given in Table I.

TABLE I. Dielectric Constants of Dilute Ethanol Solutions in Carbon Tetrachloride.

Concentration, moles/liter	Dielectric Constant			
	Series I	Series II	Series III	Average
0.01505	2.225	2.230	2.230	2.228
0.02096	2.228	2.234	2.230	2.231
0.02989	2.236	2.235	2.236	2.236
0.03694	2.237	....	2.241	2.239
0.04297	2.237	2.245	2.243	2.242
0.04521	2.241	2.244	....	2.243
0.05231	2.238	2.246	2.246	2.243
0.05552	2.241	2.244	2.245	2.243
0.05804	2.242	2.246	2.244	2.244
0.06627	2.245	2.246	....	2.246
0.07352	2.252	2.250	2.249	2.250
0.07843	2.250	2.254	2.252	2.252
0.08547	2.258	2.259	2.261	2.259

Figure 1 shows the non-linear relationship of the average dielectric constants to concentrations of ethanol solutions. The specific nature of the non-linearity of these curves is also illustrated by the fact that the best fit of the curves as indicated by the computerized analysis of variance of the regression results was a cubic equation in all cases.

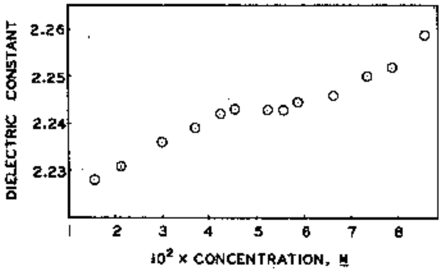

FIGURE 1. **The Non-linear Relationship Between Dielectric Constant and Ethanol Concentration in Carbon Tetrachloride.**

The shape of the curve in Figure 1, which is typical of all the series of ethanol solutions studied, is indicative of the self-association behavior. The curve has a decrease in slope beginning at about 0.04 *M*. This is interpreted as being due to the fact that at about this concentration the alcohol begins to exist to a sizable extent in the form of dimers which results in a partial cancellation of permanent dipole moment contributions to the dielectric constant. This is in accord with evidence from spectral studies. It is at about this concentration that peaks appear which are attributed to alcohol dimers (Hopkins, 1967). Going to higher concentrations produces larger aggregates which have structures in which dipole moments do not tend to cancel. The dielectric constant then rises faster as is seen in Figure 1, the slope increasing from concentrations of about 0.07 *M* upward.

It thus appears that equilibrium among hydrogen-bonded species gives rise to a significant effect on the dielectric constants of alcohol-carbon tetrachloride solutions in a range of concentration not usually examined in such detail. These effects occur at concentrations similar to those where monomer-dimer and monomer-dimer-multimer equilibria have been shown to predominate and have been studied by infrared spectroscopy.

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