Association of Ethanol in Carbon Tetrachloride

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AN attempt has been made to resolve the controversy existing with regard to both the mode of association of n-alcohols in non-polar solvents,[1] and the nature of the solute polarisation–concentration plots for such solutions.[2]

The dependence of dielectric constant, ϵ, and solute polarisation, P, on the concentration of a series of solutions of ethanol in carbon tetrachloride has been determined, and the near-infrared spectra of the same solutions examined.

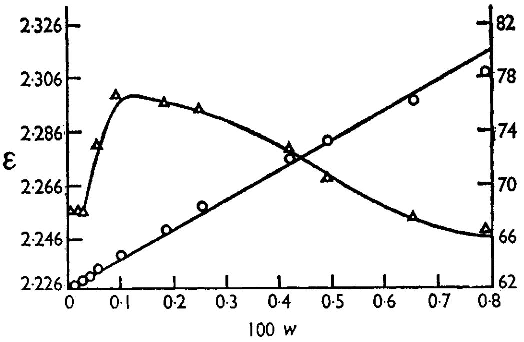

FIGURE 1. *Ethanol in carbon tetrachloride. Variation of dielectric constant* (ϵ, ○) *and solute polarisation* (P, △) *with ethanol weight fraction,* w.

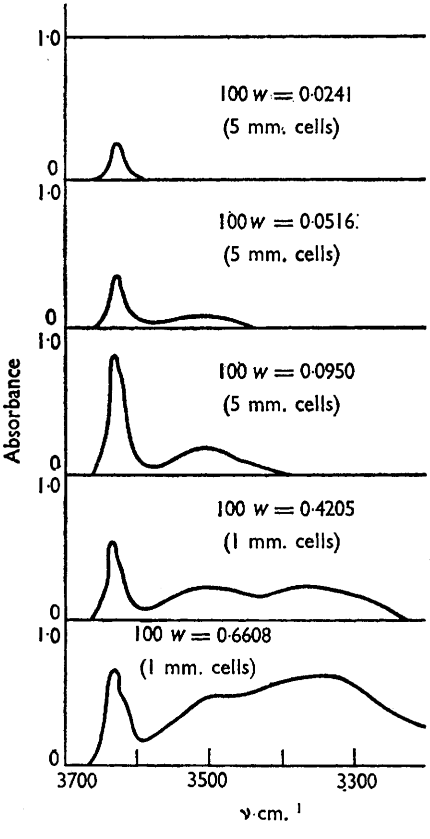

FIGURE 2. *Ethanol in carbon tetrachloride. Near-infrared spectra at various ethanol weight fractions.*

Alcohol solutions give rise to near-infrared absorption bands at approximately 3640, 3500, and 3350 cm.$^{-1}$, these bands being attributed to the presence of monomer, dimer and trimer, and higher polymer respectively.[1a] The sole presence in very dilute solution of the single sharp band at 3635 cm.$^{-1}$ is indicative of the existence of monomer only, and this coincides with linear dependence of both ϵ and P with the alcohol weight fraction, w (Figs. 1 and 2). Increasing w causes positive deviations in ϵ and P, and the onset of this effect coincides with the appearance of the absorption band at 3520 cm.$^{-1}$ which is due to the presence of dimers and trimers in solution. At a value of w of about 0·001, a maximum occurs in the P–w plot and this coincides with the appearance of the broad absorption band at 3350 cm.$^{-1}$ At higher alcohol concentrations, P decreases with increasing w, and negative deviations appear in the ϵ–w plot. Positive or negative deviations in the ϵ–w plot can be explained if the dipole moments of the individual monomer units in the polymer are reinforced or are in partial opposition respectively. It is concluded therefore, that the lower polymers responsible for the band at 3520 cm.$^{-1}$ are linear, and the higher

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[1] (a) G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, 1960. (b) U. Liddel and E. D. Becker, *Spectrochim Acta.*, 1957, **10**, 70. (c) W. C. Coburn and E. Grunwald, *J. Amer. Chem. Soc.*, 1958, **80**, 1318, (d) J. L. Grove, Ph.D. Thesis, Pennsylvania State Univ., 1957.

[2] J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955; R. J. W. Le Fèvre and A. J. Williams, *J. Chem. Soc.*, 1960, 108.

polymers responsible for the band at 3350 cm.$^{-1}$ are cyclic.

On the basis of this evidence association constants for the formation of the various polymers have been determined using the methods outlined by Rossotti and Rossotti.[3] The experimental data were fitted by equations applicable to a system containing monomer, linear dimer and trimer, and cyclic tetramer only and the association constants for the three latter species are found to be 0·95 ± 0·15 mole^{-1} l., 95 ± 10 mole^{-2} l.^{2}, 650 ± 100 mole^{-3} l.^{3} respectively.

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[3] F. J. C. Rossotti and H. Rossotti, *J. Phys. Chem.*, 1961, **65**, 926.