E2-34: Nature of solvent-solute interactions of probes used in solvent polarity scales

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Many solvent polarity scales have been developed to unravel the nature of solvent-solute interactions of solutions. Widely used solvent scales when correlated with relative permittivity of solvents (E) showed that solvents fall into 3 categories: hydrogen bonding (HB), dipolar aprotic (DA),and non-polar (NP) solvents.

Using computer aided regression analysis techniques, various appropriate functions of 'ϵ' were tried out with corresponding E_T polarity scale values to obtain the best function that correlated well with E_T. These functions reveal, the types of interactions predominant in each class of solvents. In HB solvents charge cloud type of interactions are indicated while in the DA solvents presence of extensive polarizations are shown.

This paper deals with a new correlation related to widely used solvent polarity scales.

Several attempts have been made to understand solute solvent interactions in solvent polarity scales by many workers, the most recent being that of Marcus. He used the E_T scale with a linear free energy relationship involving Kamlet-Taft type equation. However this requires several parameters such as hydrogen bonding donor and acceptor abilities and polarizabilities of solvents and these cannot be obtained accurately.

The use of relation permittivity (ϵ) of a solvent avoids the use of such various solvent parameters. We have correlated several widely used solvent polarity scales (E_T scale and Z-values) with relative permittivities of solvents and in each correlation solvents naturally fall into 3 distinct classes.

Dimroth *et al* E_T polarity scale was used to probe the solute solvent interactions with varying functions of ϵ as Marcus too had selected this scale.

Several functions of ϵ were tried out with E_T values for each class of solvents, in particular HB solvents and DA solvents. Conventional way of assuming the exsistence of various types of coulombic forces was found to be unsatisfactory. However, detailed regression analysis using Debye-Huckel type of functions yielded better results.

Details of the functions and regression analysis data will be presented.

A function of ϵ emulating the type of Debye Huckel expression was tried with HB and DA classes of solvents. HB solvent yielded very good correlation giving regression coefficient of nearly 90%, thus indicating the existence of coulombic interaction of the type envisaged by Debye-Huckel charge cloud. This shows the solvent dipoles with H-bonding ability around the solutes to be extensively aligned, extending well over the first solvation shell, thus giving a new picture for the solvation of a solute with solvents having permanent dipoles. However, this function was found to be unsatisfactory for the DA solvents; a function involving polarizability, correlated well with them.