CHAPTER I

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The important role played by hydrodynamic measurements in providing information regarding the molecular weight, size, shape and conformation of the macromolecules cannot be over-emphasized. For deducing such information from the numerical values of the quantities like sedimentation coefficient, diffusion coefficient, intrinsic viscosity, etc., it is important to understand the dependence of these quantities on the shape and size for models which are structurally close to the real molecule.

During the last twenty-five years there has been a tremendous progress in the field both from the experimental and theoretical points of view. On the experimental side many improved versions of the instruments are now available. New techniques using optical methods have facilitated the measurements of diffusion coefficients. Viscometers with very small shear rates have been developed.

On the theoretical front the progress is equally impressive. The molecules are no longer treated only as spheres, ellipsoids of revolution, the rigid rods and random coils. More realistic models have been considered taking into account the internal rotation, flexibility of molecules and the excluded volume effect between different segments (sub units) of the molecule.
Comparatively lesser amount of work has been done concerning the hydrodynamic properties of small molecules because of their lesser practical importance. But for comparison between experiment and theory, it seems to be more advantageous to work with molecules of known structures in which the atomic details are known and their behaviour in solutions is understood. The diffusion coefficients of a number of n-alkanes have been measured recently and the results have been compared with Kirkwood theory.

In the present work we report the intrinsic viscosity of some n-alkanes. These are extended to two other series, viz., n-alcohols and fatty acids in order to evaluate the effect of minor structural changes at the end of the chain. Diffusion coefficients for some of the acids were also measured. The results have been discussed in terms of recent theories.

While determining the densities of the solutions, required for viscometric work, it was thought worthwhile to extend these measurements to higher concentration ranges also (mole fraction 0 to 1) in order to find the excess volumes of mixing. These along with other excess properties measured by other workers, give supplementary information regarding the behaviour of the molecules in different solvents (benzene and carbon tetrachloride).