A New Statistical Mechanical Model for Calculating Kirkwood-Factors in Self-Associating Liquid Systems

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Dielectric properties of liquids and liquid mixtures are usually described on the basis of the Onsager-Kirkwood Theory. For many non-polar and polar systems this theoretical concept is most successful to describe electric susceptibilities and dielectric constants using the so-called apparent dipole moment, which contains the Kirkwood-factor as an adjustable parameter. However, a consistent quantitative description of the Kirkwood-factor in case of highly correlated molecules such as hydrogen-bonded liquid systems is still missing.

We present a new and consistent theoretical model to predict Kirkwood factors gK of alcohol + hydrocarbon mixtures as function of the mixture composition. It is shown, how linear self association as well as ring-like formation of associated species can be accounted for in frame of a multi-step quasi-chemical association model leading to Kirkwood factors gK ranging between 1 in very dilute solutions of alcohols in hydrocarbon up to values higher than 3 as observed experimentally in pure alcohols. The appearence of a minimum for the Kirkwood factor ($gK < 1$) at mole fractions of the alcohols around 0,1 – 0,2 is well described in accordance with experimental results.