

## Dielectric Constant of Dipolar Liquids from Perturbation Theory

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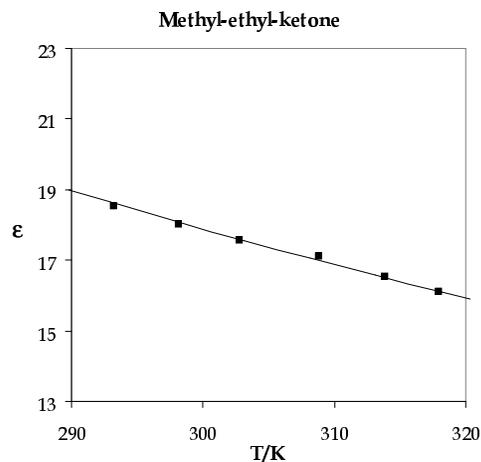
For better understanding the structure of electrolyte solutions, the knowledge of the dielectric properties of the solvent has a fundamental importance. The solvent usually is a polar liquid, generally water. The most important dielectric property of a polar fluid is the relative permittivity that is used in the electrolyte models.

In order to calculate the relative permittivity we used the Kirkwood-Fröhlich equation. The Kirkwood-Fröhlich equation takes care of the short range correlations by introducing the Kirkwood  $g$  factor ( $g_K$ ). In the statistical mechanics of dipolar fluids estimation of  $g_K$  is essential, although it is very problematic.

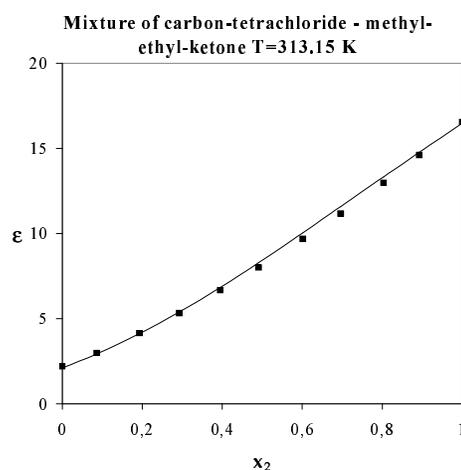
At the moment there is no accurate physically based method for the calculation of the dielectric constant of a real polar fluid. In this presentation we use the non polarizable dipolar hard sphere fluid as a model and second order perturbation theory to calculate the  $g$ -factor. The intermolecular potential between the molecules divided into a reference and a perturbation part. The reference system is the hard sphere fluid and the perturbation part include the dipole-dipole interaction.

We assume that the calculated  $g$ -factor is good for polarizable hard sphere molecules as well, and on the basis of the Kirkwood-Fröhlich equation we propose an empirical extension of the theory to take into account the polarizability. We use a series expansion of the Kirkwood-Fröhlich equation for  $\epsilon$  as a function of dipole strength function and, on the basis of a free energy based treatment, show that this series expansion is reasonable. The free energy route provides the dielectric constant on the basis of the dielectric response to an imposed weak electric field.

The theory can straightforwardly be extended for mixtures. On the basis of the results for pure fluids, where the dipole moment of the molecule is adjusted by fitting the theoretical curve to the experimental data, we give estimations for the molecular parameters that we use in the calculations for mixtures. Our results are in good agreement with experimental data for carbonyl compounds as the figures show.



**Fig. 1.** Relative permittivity vs. temperature for methyl-ethyl-ketone. The solid curve represents the expansion of the Kirkwood-Fröhlich equation, while the squares are experimental data.



**Fig. 2.** Relative permittivity vs. mole fraction for carbon tetrachloride – methyl-ethyl-ketone mixture at T=313.15 K. Presentation as for Fig. 1.