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## 1 Introduction

High temperature liquid chromatography is a variant of classical liquid chromatography. Here, the mobile and stationary phases are heated up to temperatures above the normal boiling point. Although temperature can be controlled very easily and hence, temperature can be incorporated into method development to speed up analysis time or influence the selectivity of a separation, physico-chemical data about the temperature dependent behaviour of water-organic solvent mixtures is hard to find. Therefore, the aim of a joint research project was to gather information about the temperature dependence of the **viscosity**, the **vapour pressure** and the **static permittivity** of **water – organic mixtures** comprised of **water** and an organic solvent like **acetonitrile**, **methanol**, **tetrahydrofuran**, **ethanol**, **isopropanol** and **acetone**.

## 2 Results and Discussion

### 2.1 System pressure

When the temperature is increased above the normal boiling point of the solvent, a phase transition of the mobile phase in the system must be prevented. **Figure 1** shows the system pressure for the system water-methanol in dependence on temperature. At 200 °C, the system pressure is about 40 bar which is the highest vapour pressure observed for all solvent mixtures defined above. In **Figure 2**, different solvent systems are compared in terms of their system pressure at 150 °C. The data have been correlated with NRTL model. As can be seen from **Figure 1** and **2**, the experimental data can be very well described with the calculated data.

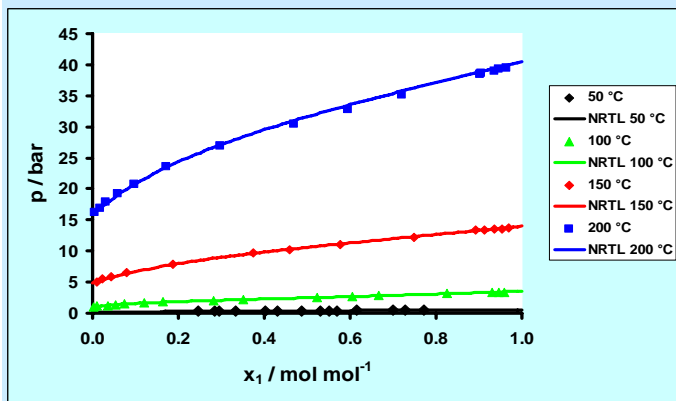


Figure 1: System pressures for the solvent mixture methanol (1) and water (2) at different temperatures.

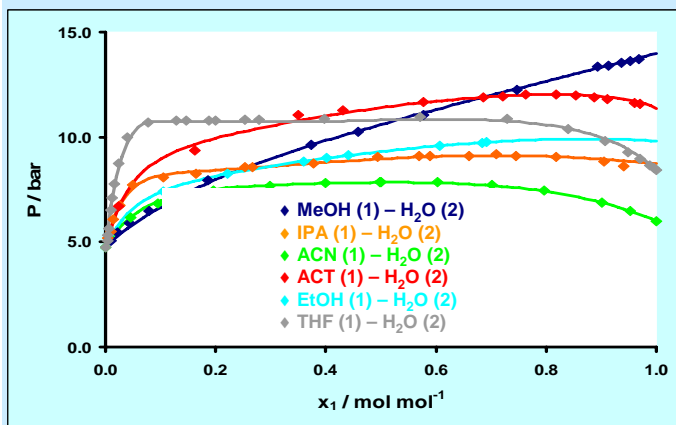


Figure 2: System pressures for different solvent mixtures at 150 °C, data correlated with NRTL.

### 2.2 Viscosity

Data about the viscosity is essential to calculate the pressure drop over a particle packed column or over a capillary connecting different HPLC modules. Although there are some approaches to theoretically predict the viscosity at different temperatures, until now there is no physico-chemical model which can be used for the prediction of the viscosity of a binary solvent mixture in dependence on temperature and the composition. Some approaches like the Arrhenius model do not consider the large viscosity deviations which are observed for mixtures comprised of water and an organic solvent as it is typical for reversed phase HPLC. Also, there are only very limited data in the scientific literature. Hence, the experimental measurement of the viscosity of binary eluent mixtures in dependence on temperature and composition has been accomplished during the project using a capillary viscometer. **Figure 3** shows the viscosity of the system isopropanol (1) and water (2). It can be clearly seen that there is a huge maximum at 30 °C. In contrast to this, at 100 °C this maximum is vastly reduced. This means that even mobile phases consisting of water and a higher chain alcohol can be used with sub 2  $\mu$ m particle packed columns on conventional HPLC systems with a pressure limit of 400 bar.

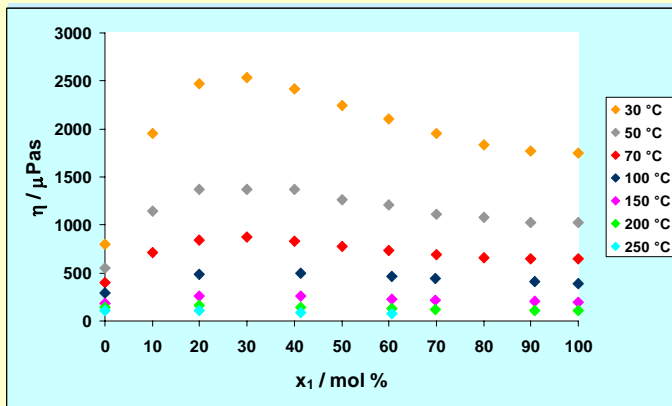


Figure 3: Viscosity for the solvent mixture isopropanol (1) and water (2) at different temperatures. Data at 30, 50 and 70 °C from M. Moha-Ouchane, C. Boned, A. Allal, and M. Benseddik: *Viscosity and Excess Volume at High Pressures in Associative Binaries*; International Journal of Thermophysics, Vol. 19 No. 1, 1998, pp. 161-189

### 2.3 Static permittivity (dielectric constant)

When the temperature is increased, the polarity of a solvent mixture is influenced. In liquid chromatography this effect can be used to effectively change the selectivity of the phase system, to replace organic solvents with water and to use temperature gradients instead of solvent gradients.

The experimental set-up for measuring the static permittivity at temperatures up to 200 °C has been accomplished by using a capacitive measurement method integrated into a pressurized cell and is depicted in **Figure 4**.

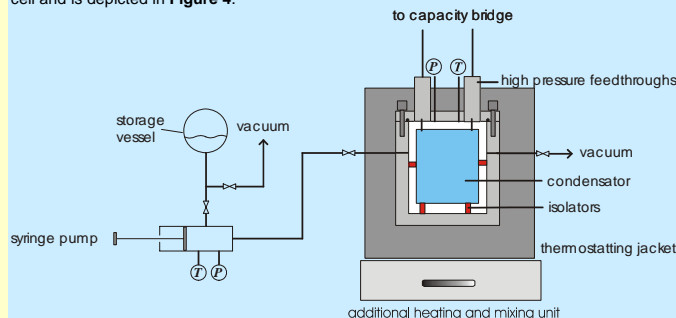


Figure 4: Schematic illustration of the experimental set-up for the measurement of the static permittivity.

**Figure 5** shows the dependence of the static permittivity on temperature and composition for the system acetonitrile (1) and water (2). Also, the static permittivities of the pure solvents can be compared in this representation. Pure water has a very high static permittivity at 25 °C, which drops from 80 to 35 when the temperature is increased to 200 °C. This is a huge difference when compared to pure acetonitrile, whose static permittivity decreases from 40 at room temperature to 18 at 200 °C. This information can now be used to construct nomographs in order to predict the solvent strength at different compositions of the mobile phase.

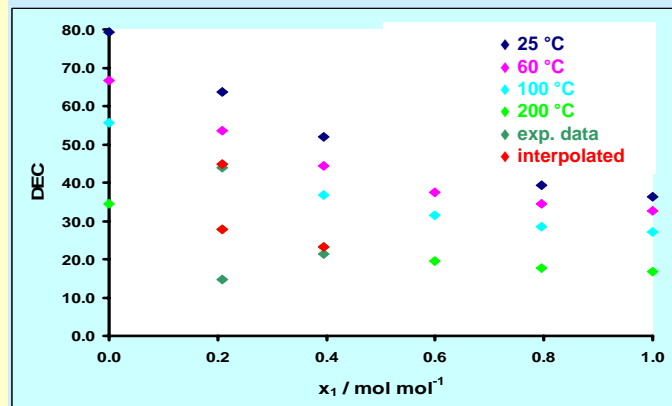


Figure 5: Static permittivity of the system acetonitrile (1) and water (2) at different temperatures.

## 5 Acknowledgements

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