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Multicomponent Diffusion Coefficients in Liquids from Model-Based Raman Spectroscopy

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1. Introduction

Today, diffusion coefficients in liquids still cannot be predicted with sufficient accuracy due to a lack of measurement data. Since established diffusion experiments require strongly increased effort in multicomponent mixtures a new diffusion measurement technique has been developed by the authors to make the determination of multicomponent diffusivities more practically tractable. The new experiment employs quantitative 1-D Raman spectroscopy and model-based methods for experimental design and data analysis. It has been validated for binary mixtures [1] where the full concentration dependence of the diffusion coefficient could be recovered from one short experiment [2]. Measurements in multicomponent mixtures have now been obtained.

Model-based Raman diffusion experiments will be briefly introduced in the next section. Recent results on multicomponent diffusion experiments will be discussed in Section 3. Finally, some general conclusions on the new approach will be given.

2. Model-based Raman diffusion experiments

Established diffusion experiments are commonly based on refractive index or conductivity measurements which cannot unambiguously be related to the individual concentrations in multicomponent mixtures. Thus, several experiments are necessarily required for the analysis. In contrast, spectroscopic techniques simultaneously determine all species in a mixture. Therefore, a quantitative one-dimensional Raman spectroscopy technique was developed which yields the mole fractions of all diffusing components with high spatial and temporal resolution. Spectra are analyzed using the indirect spectral hard modelling approach [3] reducing calibration effort and allowing the analysis of nonideal spectra.

Raman diffusion experiments are conducted in a vertical column similar to those employed in interferometry. Initially, two layers of solutions with slightly different composition are formed. Mixing then occurs by diffusion. The concentration evolution is observed in a part of the diffusion cell by Raman spectroscopy.

Model-based methods are employed to ensure optimal experimental design and procedure as well as for data analysis. A more detailed description of the Raman diffusion experiment can be found in [1,2].

3. Multicomponent diffusion experiments

The new Raman diffusion experiment was validated for ternary mixtures by comparison with data from [4] for an equimolar mixture of n-Propanol+1-Chlorobutane+n-Heptane [5]. It could be shown that the Fick diffusion matrix can be determined from a *single* Raman diffusion experiment. Practically, experimental effort could be more than halved by the new approach compared to established techniques.

The Raman experiment allowed for a straightforward extension to quaternary systems since general design rules were derived and precision of the mole fraction measurements is largely retained. Reliable diffusion coefficients could be determined from three experiments for an equimolar mixture of Cylohexane+Toluene+1,4-Dioxane+Chlorobutane.

Recently, diffusion in a quinternary mixture where vinyl acetate has been added to the above quaternary system could be observed. Mole fraction data for Cyclohexane is shown in Figure 1. Results are similar for the other components.

It is found that the measurement error is basically identical to the quaternary case (σ=7e-4). Thus, the new model-based Raman diffusion experiment may render the determination of diffusivities in five component systems for the first time possible.

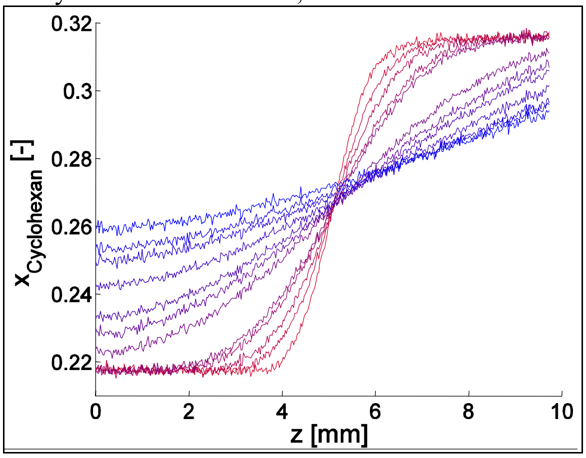

Figure 1: Cyclohexane mole fraction in a quinternary diffusion experiment.

4. Conclusion

A new diffusion experiment based on Raman spectroscopy and model-based methods has been developed. The new approach allows for efficient and reliable determination of diffusion coefficients in multicomponent mixtures. Further applications to electrolyte solutions and polymer distributions in hydrogels have already been successful [6].

References

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