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Fluid Phase Equilibria 228–229 (2005) 357–366
FLUID PHASE EQUILIBRIA
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Concentration-dependent diffusion coefficients from a single experiment using model-based Raman spectroscopy

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Abstract

Diffusion in liquids can still be predicted only with high uncertainty due to the lack of sufficient experimental data. Diffusion experiments are complex and time-consuming. Furthermore, the concentration dependence of the diffusion coefficients requires usually several experiments even for binary mixtures. The possibility to extract this information from *one short* Raman diffusion experiment is explored here. A general identification framework is provided which does not require the a priori specification of a diffusion coefficient model structure but establishes the concentration dependence directly from the data. The methodology is used to determine the diffusion coefficient in the mixture ethyl acetate–cyclohexane in a wide concentration range.

Keywords: Diffusion coefficient; Spectroscopy; Experimental method; Inverse problem

1. Introduction

Even in binary liquids, the concentration dependence of the diffusion coefficient is not simple and no single predictive correlation gives satisfactory estimates for all mixtures [1]. Therefore, experiments are usually necessary in order to determine precise diffusion coefficients required in mass transfer calculations. Unfortunately, most diffusion experiments are rather complex and time-consuming [2]. Furthermore, only constant diffusion coefficients describing the behavior at one single composition are usually determined. A number of experiments are therefore needed to describe the overall concentration dependence.

On the other hand, the direct determination of concentration dependent multicomponent diffusivities from a single diffusion experiment was already suggested more than 30 years ago [3]. For binary diffusion in liquids, this idea has been implemented using diaphragm cell [4] and interferometry measurements [5]. In diaphragm cell experiments, the diffusion coefficients found are always time and concentration averaged values [2]. From this data, Clunie et al. [4] retrieved information about the first and second derivative of the diffusion coefficient with respect to concentration. Thereby, the concentration dependence may be described in an interval adjacent to the measured composition. The values determined by this method show a large scatter though and several experiments are still required to analyze the full composition space. In the analysis of holographic interferometry experiments, a polynomial for the concentration dependence of the diffusion coefficient $D(c)$ was proposed [5]. The coefficients of this polynomial were then estimated from the data in a least squares procedure. In experiments, only linear and quadratic functions were used. It was found that the correlation among the coefficients was too severe to allow them to be determined with sufficient precision. This led to abandonment of this idea. The possibility of direct determination of the concentration dependence is therefore not even mentioned any more in later reviews on measurements of diffusion coefficients [2,6] despite its prospect of reducing experimental

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doi:10.1016/j.fluid.2004.08.017

effort substantially. More recently though, this possibility was exploited in other fields such as adsorption [7] and transport in anionic gels [8].

In this work, the estimation of concentration dependent diffusion coefficients in binary liquids will be reexamined. Recently, a new measurement technique for diffusion in liquids using model-based Raman spectroscopy has been presented by the authors [9]. The new technique is designed to reduce experimental effort for diffusion measurements. It was shown that the concentration dependence of the diffusion coefficient could be determined from the joint analysis of four Raman experiments. As a drawback a diffusion coefficient model structure (e.g., a polynomial of fixed order) had to be postulated a priori as in the work of Durou et al. [5]. This may be unsatisfactory: if the suggested structure is not capable of capturing the concentration dependence properly, the estimate may be misleading and the model will not adequately describe the data. If a very flexible model structure is used, a large number of parameters have to be determined which is prohibitive due to the computational effort and the ill-posed nature of the identification problem.

Recently, an incremental model identification strategy has been developed by some of the authors for the determination of concentration dependent diffusion coefficients directly from the data, i.e., without a priori specification of a model structure [21]. In this simulation study, complicated diffusion coefficients with several extrema could be estimated within 5% error. In the following, the approach will be applied to actual data from Raman diffusion experiments.

Raman diffusion experiments will be briefly introduced next and some recent improvements are discussed. Subsequently, the mathematical description of the diffusion experiment is presented. This model is then employed in the incremental identification procedure. Results will be presented for the mixture ethyl acetate–cyclohexane and compared to literature data [11].

2. Experiment

The diffusion experiments in this work were conducted employing one-dimensional Raman spectroscopy. A first description of the experimental setup was given by the authors in [9,12]. Here, the principle is summarized and we report some recent improvements.

The Raman diffusion experiment is performed in a vertical column similar to those used in interferometric diffusion experiments [2]. Initially, two uniform solutions of different composition are layered on top of each other. Mixing then occurs due to diffusion. The mole fractions of all species $\tilde{x}_i(z, t)$ are simultaneously measured in a section of the diffusion cell with high spatial and temporal resolution using Raman spectroscopy.

In order to induce the so-called Raman scattering the beam of an Argon Ion Laser (SPECTRA PHYSICS, excitation wavelength 514.5 nm, power 1.5 W) is focussed and directed vertically through the diffusion cell made of quartz-glass, as shown in Fig. 1. Molecules in the sample get excited and emit Raman scattering. The frequency of the Raman signal is shifted compared to the incoming laser beam. The signal is collected in a 90° angle to the cell and the dominating, disturbing Rayleigh scattering is removed by filtering. An imaging spectrograph (ARC Spectra Pro 500 i) equipped with a 1200 l/mm grating resolves the spectral information. In this way, a two-dimensional image with one spatial and one spectral coordinate is obtained. The image is detected by an air-cooled charge coupled device (CCD) camera (PRINCETON INSTRUMENTS NTE/CCD-1340/400) and stored sequentially on a PC. Thus, each detector row (e.g., no. 1, 2 in Fig. 1) collects the emitted Raman scatter from a certain volume along the measurement line. From this spectral information, the concentration profiles of all species are determined as described below.

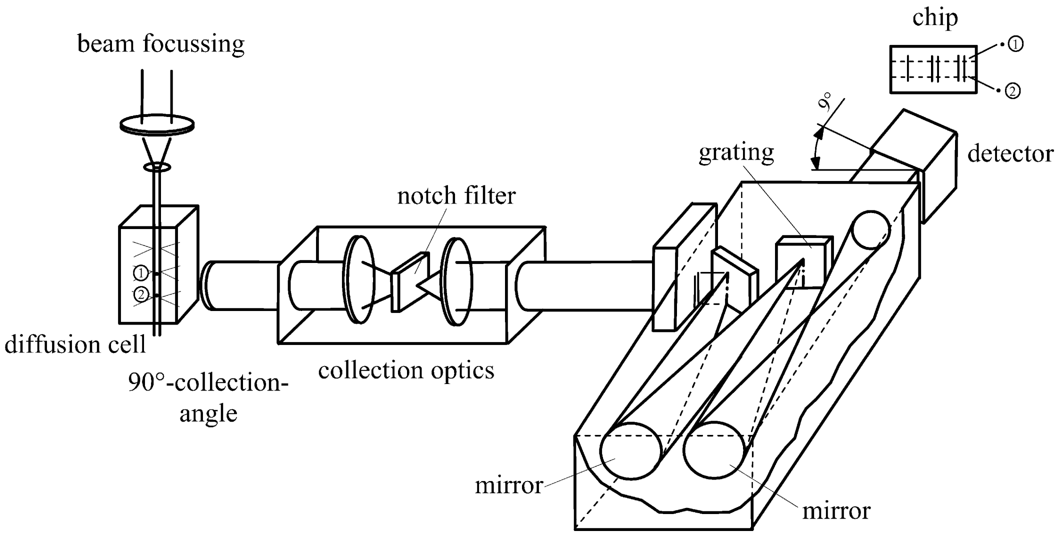

Fig. 1. Experimental setup of one-dimensional Raman spectroscopy for diffusivity measurements.